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Computational Insights into the Acceptor Chemistry of Phosphenium Cations

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Phosphines are traditionally considered as Lewis bases or ligands in transition metal and main group complexes. Despite their electron-rich (lone pair-bearing) nature, an extensive coordination chemistry for Lewis acidic phosphorus centers is being developed; such chemistry provides a new synthetic approach for phosphorus–element bond formation, leading to new types of structures and modes of bonding. Complexes of Ph_2P^+ with a variety of donor elements (P, N, C) give experimentally short donor–acceptor bond lengths, when compared to other cationic phosphorus Lewis acid complexes. We have calculated that the energy of the lowest unoccupied molecular orbital (LUMO) in Ph_2P^+ is lower than that of $(Me_2N)_2P^+$, which partially explains the greater exothermicity of reactions of donors with the diaryl acceptor. Furthermore, the energies required to distort the diphenylphosphenium cation from its ground-state geometry are significantly smaller than those of the diamido cations and, thus, enhance the exothermicity of donor coordination. These computational data, in conjunction with evidence from experimental solid-state structures, indicate that Ph_2P^+ is a significantly better Lewis acid relative to the more common diaminophosphenium analogues $(R_2N)_2P^+$ and are used to elucidate the nature of the bonding in donor–phosphenium complexes.

1. Introduction

The labels “donor” or “ligand” for electron-rich (defined as “lone pair”-bearing) phosphines in coordination chemistry is somewhat misleading in the context of the developing series of compounds involving coordinatively unsaturated phosphorus compounds as Lewis acids. Complexes of phosphorus cations[1] with arene,[2] carbene,[3] amine,[4,5] imine,[6] phosphine,[7−9] and gallanediyl[10] ligands have been reported, demonstrating the versatility of coordination chemistry for the synthesis of new phosphorus−element (P−E) bonds and for the potential formation of new bonding environments for phosphorus.

A few general synthetic approaches have been used to obtain donor−phosphenium complexes. For stable phosphenium salts (typically diaminophosphenium salts)[11] that contain nonreactive anions, complexes can be synthesized by simply mixing a solution of the salt with a Lewis base.[12] More recently, a new, and perhaps more general, protocol has been developed for the synthesis of adducts of unstable dialkylphosphenium or diarylphosphenium salts by the halide abstraction of a suitable halophosphine in the presence of a

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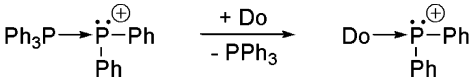
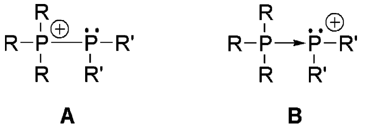
Scheme 1. Ligand Exchange for the Synthesis of New Phosphorus-Element (P−E) Bonds; Replacement of PPh_3 by a Stronger Donor (Do).



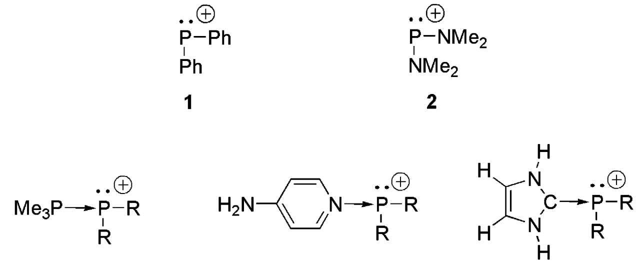
Scheme 2. Two Bonding Models for Phosphine-Stabilized Phosphenium Cations.



Lewis base, such as PPh_3.[1,13] Although intramolecular donor-stabilized phosphenium cations have been studied for more than 20 years,[14] the intermolecular donor-stabilized salts allow for the study of the chemistry of phosphenium cations with less-elaborate substitution. Furthermore, the Lewis base in such donor-stabilized phosphenium complexes can be readily displaced by substitution with a stronger donor; this final approach has been used to synthesize numerous donor−phosphenium complexes (Scheme 1).

Isolation of the free diphenylphosphenium cation has remained elusive but an extensive series of base-stabilized Ph_2P^+ complexes have been isolated and comprehensively characterized, whereas few complexes have been isolated and structurally characterized for other phosphenium acceptors.[15] In fact, the diphenylphosphenium cation has only been isolated in the presence of a donor and, although such complexes are sometimes considered to be phosphinophosphosphonium cations (**A** in Scheme 2), the reactivity shown in Scheme 1 suggests that, in this context, it is perhaps more reasonable to consider these ions to be phosphine-stabilized phosphenium cations (**B** in Scheme 2).

In contrast to dialkylphosphenium or diarylphosphenium compounds, salts of base-free bis-amino phosphenium cations are readily isolated.[11] Because of the experimental observations, most previous computational work has been centered around bis-amino phosphenium cations and, thus, provides insight only toward the more electron-rich cations.[16−18] In some computational studies, the complexation of hydride or halide donors to phosphenium cations has been used as a probe of the stability of the cations,[16,17,19] although there have also been some studies of the acceptor chemistry of parent phosphenium cation (H_2P^+),[20] and other selected complexes[21] have been reported. Given that complexes of type **B** have been shown to be synthetic sources of Ph_2P^+, a more-detailed study of the influence of the donors and substituents in such complexes is warranted. Furthermore, the differences in the structural features and reactivity[21,22] observed for analogous complexes of diphenylphosphenium and diaminophosphenium cations, in conjunction with the apparent generality of their coordination chemistry, have prompted us to investigate the relative acceptor strength of the diphenylphosphenium cation to that of the more familiar and stable diaminophosphenium cation. In this work, computational studies and comparisons to experimentally isolated examples of systems **1**−**5** are presented (Figure 1) to provide bonding descriptions for appropriate model compounds and to compare the energetics of donor−acceptor reactions of the two major classes of experimentally isolated phosphenium cations.



1 **2**

3-Ph R=Ph
3-NMe$_2$ R=NMe$_2$
4-Ph R=Ph
4-NMe$_2$ R=NMe$_2$
5-Ph R=Ph
5-NMe$_2$ R=NMe$_2$

Figure 1. Numbering scheme and drawings of the model compounds examined in this work.

2. Computational Details

All calculations were performed with the Gaussian 98 suite of programs.[23] The geometries and energies of products and reactants have been calculated using density functional theory (DFT). For the geometry optimizations, the B3PW91 method[24−28] was used in conjunction with the 6-31G(d) basis set. The geometries were restricted to the highest reasonable symmetry, and each stationary point was confirmed to be a minimum on the potential energy surface by yielding zero imaginary vibrational frequencies in the vibrational frequency

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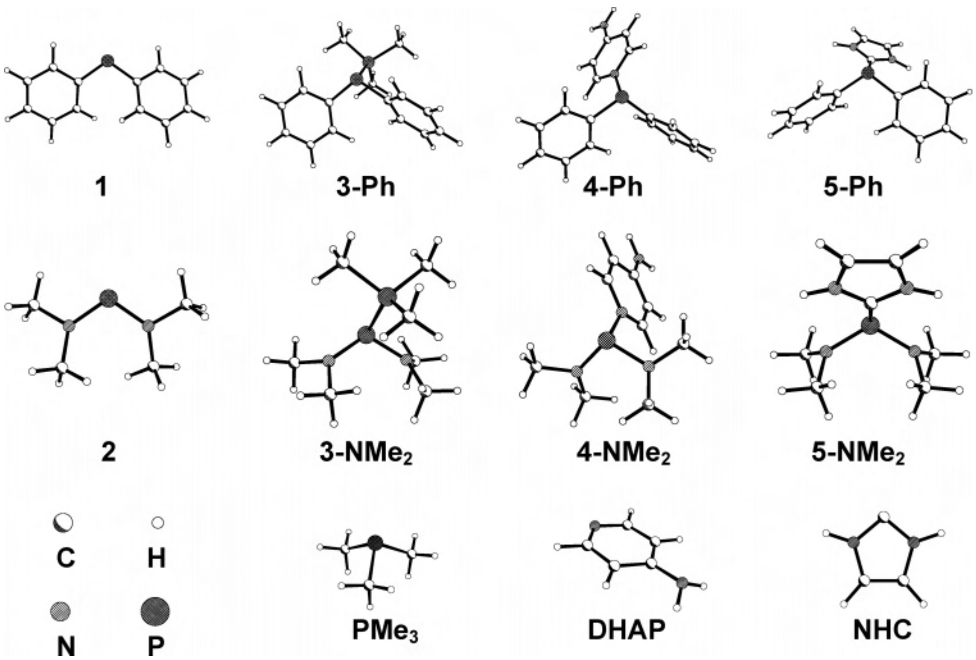

Figure 2. Selected optimized structures for cations, donors, and complexes.

analysis, unless otherwise indicated. The reported energies (E_{total}) are the single-point energies calculated with the 6-311+G(3df,2p) basis set and have been corrected by the zero-point vibrational energy (ZPVE) calculated with the 6-31G(d) basis set, scaled by the factor of 0.9774 suggested by Scott and Radom.[29] Bond energies and fragment energies were determined by single-point calculations at the B3PW91/6-311+G(3df,2p) level of theory. Depictions of selected optimized structures are found in Figure 2 and a complete listing of the calculation results, including atomic coordinates, is provided in the Supporting Information. Population analyses were performed on the B3PW91/6-31G(d) structures using the Natural Bond Order (NBO)[30] method implemented in Gaussian 98, and drawings of orbitals were prepared using MOLDEN.[31] The absolute electronegativity (χ) and absolute hardness (η) values were calculated at the MP2/6-31+G(d) level of theory, using the B3PW91/6-31G(d) geometries, following the method outlined by Gudat.[16]

3. Results and Discussion

Phosphenium cations are the isolobal and isovalent analogues of the more familiar singlet carbenes of organic chemistry. In this light, each of these species has a formally sp^2-hybridized central element and a lone pair of electrons in a σ-type orbital, as well as an unhybridized, empty ***n***p π-type orbital. Because of this electronic structure, such species are expected to be both amphiphilic and amphoteric. Although the donor/base chemistry of stable carbenes[32] and phosphenium cations[7,16,33] has been investigated extensively, the acceptor/acid chemistry of these compounds has remained relatively underappreciated. The acceptor chemistry of transient (generally triplet) carbenes has been exploited extensively, because the complexes of donors with carbenes comprise the ubiquitous and useful family of Wittig reagents that are used in organic chemistry.

In such isovalent carbenic systems, the P center has a greater effective nuclear charge, a positive molecular charge, and a larger size than carbon; thus, one would predict that phosphenium cations should have a richer acceptor chemistry than their diagonal relatives. In the case of singlet carbenes, this prediction is borne out experimentally, in that there are virtually no structurally characterized examples of stable carbenes acting unambiguously as acceptors,[34-36] whereas there is now a bourgeoning acceptor chemistry of phosphenium salts.[15]

In this work, we wish to assess the acceptor ability of phosphenium cations that are bonded to the two most common types of functional groups studied experimentally. Phosphenium cations bearing two alkyl or aryl substituents (weakly π-electron-donating and σ-electron-donating), such as the diphenylphosphenium cation **1**, are typically very reactive and have only been isolated through Lewis base stabilization[1,37-39] of the vacant 3p$_\pi$ orbital. In contrast, the vast majority of isolated base-free phosphenium cations consists of the cationic P$^{\text{III}}$ center previously described,

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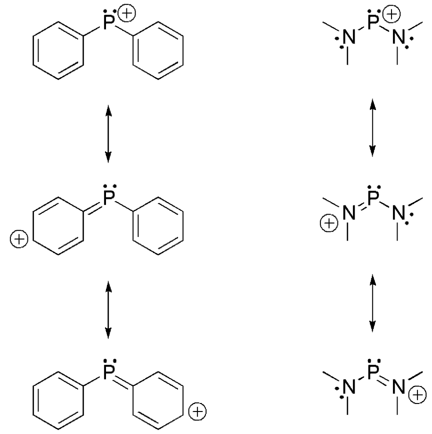
Scheme 3. Canonical Structures Showing Possible π-electron Delocalization for the Diphenylphosphenium Cation and the Bis(dimethylamino)phosphenium Cation Models Used in This Work.



1 **2**

flanked by two amido fragments (strongly π-donating and σ-withdrawing), such as the bis(dimethylamino)phosphenium cation **2**. The stability of cations of that general description is attributable to the delocalization of the lone pairs on the N atoms into the formally vacant $3p_\pi$ orbital to make a hetero-allylic 3-center 4π-electron system, in concert with the strong (−)(+)(−) polarization of the N−P−N unit.[16] Orbital interactions of this type populate the vacant $3p_\pi$ orbital (which should reduce the acceptor capability of the P atom) and favor the singlet ground state—this is the approach that has also been used typically to obtain stable carbenes and their analogues. Although the canonical structures in Scheme 3 seem to suggest that similar delocalization may be possible for **1**, the donation of π electron density from the phenyl substituents results in disruption of the aromatic π-system and is, thus, less favorable. The results detailed below allow us to quantify such a qualitative interpretation.

3.1. Free Cations. Calculated structural features for the model cations **1** and **2** are consistent with the experimental observations and, thus, the computed orbitals and energies (see Table 1) provide insight into the features that determine the relative acceptor abilities of such cations.

In the determination of acceptor properties, the most important frontier orbital is the lowest unoccupied molecular orbital (LUMO). The LUMO energy for **1** is lower than that of **2**, because of the ineffective π interaction of the phenyl π-orbitals with the vacant $3p_\pi$ orbital on the P atom in Ph_2P^+. First, as shown in Figure 2, the lowest energy structure is of C_2 symmetry and has phenyl substituents that are not coplanar (the planar C_{2v} structure is a transition state with one imaginary frequency)—such an arrangement reduces the effective overlap of the molecular orbitals (MOs) on the phenyl groups with the $3p_\pi$ orbital on the P atom. Second, even if the phenyl groups were coplanar, delocalization of the π-system would require the loss of aromaticity in the phenyl substituents. A generalized diagram illustrating the important ligand and P orbital interactions is shown in Figure 3 and depictions of the MOs formed from these combinations (and their calculated energies) are compiled in Figure 4.

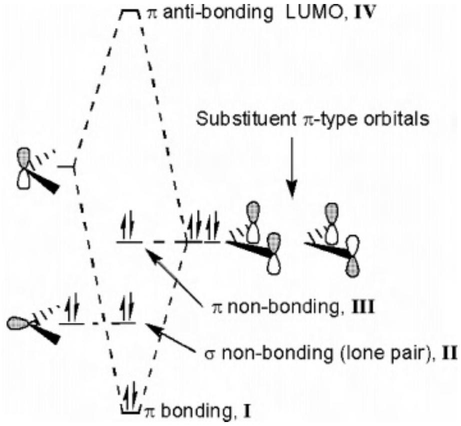


Figure 3. Generalized molecular orbital (MO) diagram emphasizing important orbital interactions. The nature of the substituents at phosphorus alters the order of the MO energies.

Although there is clearly some interaction between the π-system on the phenyl groups and the $3p_\pi$ orbital on the P atom, as evidenced by MO 23b in Figure 4, overall, the relatively small magnitude of the interaction leaves the LUMO (MO 24b, which is the most antibonding π-orbital combination) at a lower energy than that in **2**. The smaller magnitude of the π-delocalization in **1** is also indicated by the NBO populations determined for the $3p_\pi$ orbital on the P atoms in **1** (0.569 e^-) and **2** (0.690 e^-), which are both significantly greater than those calculated for Me_2P^+ (0.209 e^-) and H_2P^+ (0.002 e^-) at the same level of theory.[40] Overall, the presence of the more effective π-donor and σ-withdrawing substituents in **2** significantly alters the ordering of the MOs; particularly noteworthy is the change in the relative position of the "lone pair" orbital 16a (**II**), which is considerably more stable in **2** than the corresponding orbital in **1** (23a). Although it is not the focus of the present study, note that the relative HOMO energies of **1** and **2** suggest that Ph_2P^+ should be a considerably better donor than $(Me_2N)_2P^+$.

In contrast, the dimethylamino substituents in cation **2** are almost coplanar (also in C_2 symmetry), which allows the formally filled 2p atomic orbitals on the N atoms to interact more effectively with the $3p_\pi$ orbital centered on the P atom, as illustrated by the energy differences between the most bonding (23b for **1**, 15b for **2**) and the most antibonding (24b for **1**, 16b for **2**) π-molecular orbitals. A consequence is that the LUMO (**IV**) in **2** is considerably destabilized, with

Table 1. Calculated Data for Uncomplexed Cations

cation	symmetry	corrected energy, E_{total}[a] (au)	E_{HOMO} (eV)	E_{LUMO} (eV)	proton affinity, PA (kJ/mol)	absolute electronegativity, χ (eV)	absolute hardness, η	q(P)[b] (au)
1	C_2	−804.13235	−11.370	−8.257	446.6	9.10	4.01	1.08
2	C_2	−610.08047	−11.719	−6.910	305.0	9.20	5.63	1.34

[a] $E_{\text{total}} = E_{\text{calculated}} + 0.9774(\text{ZPVE})$. [b] Natural bond order (NBO) charge on the P atom.

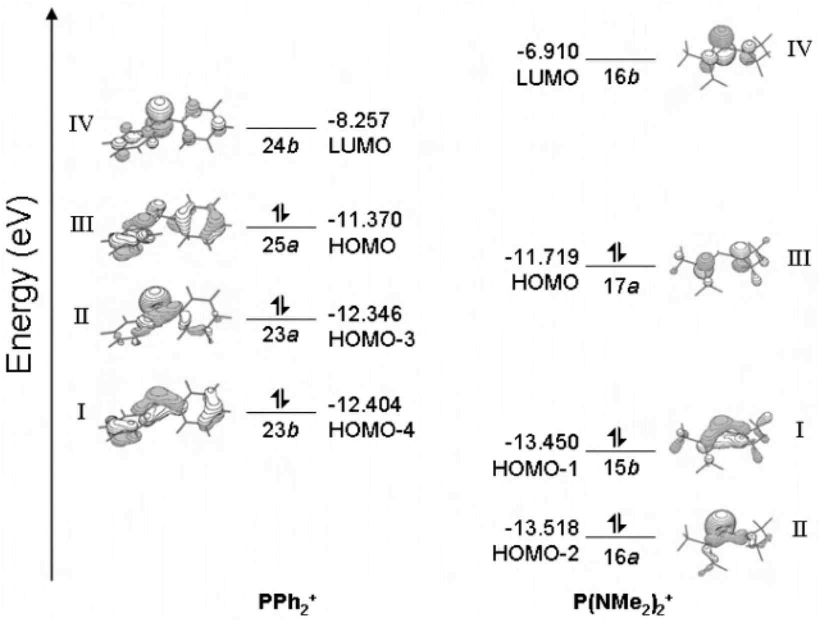


Figure 4. MO diagram for Ph_2P^+ and $(Me_2N)_2P^+$ illustrating the orbital energy levels. The orbital energies are reported in electron volts (eV) and are not plotted to scale.

Table 2. Energies and Properties Calculated for the Uncomplexed Donor Molecules

donor	symmetry	corrected energy, E_{total}[a] (au)	E_{HOMO} (eV)	ΔH_{prep} Adduct (kJ/mol)[b] with **1**	with **2**	proton affinity, PA (kJ/mol)	absolute electronegativity, χ (eV)	absolute hardness, η	pK_a[c]
PMe_3	C_3	−460.97236	−6.208	27.7	23.1	−963.3	3.70	5.29	8.65[d]
DHAP	C_s	−303.52756	−6.536	10.3	9.5	−992.8	3.64	5.35	9.11[e]
NHC	C_{2v}	−226.09770	−6.116	8.3	8.9	−1060.1	3.48	5.38	27.4[f]

[a] $E_{total} = E_{calculated} + 0.9774(ZPVE)$. [b] The preparation energy for the donor is calculated for the process "donor → donor*": $\Delta H_{prep} = E_{donor*} - E_{donor}$, where the asterisk (*) indicates that the donor fragment is in the exact same geometry observed in the coordination complex. [c] pK_a in H_2O at 25 °C; the value reported is for the carbene *N,N′*-dimethyl-imidazol-2-ylidene. [d] Data from Streuli.[44] [e] Data from Weast.[45] [f] Data from Magill et al.[46]

respect to that of **1**, and renders the population of this orbital less energetically favorable; this prediction is consistent with the relative stability of Ph_2P^- anions and paucity of $(R_2N)_2P^-$ anions observed experimentally.

Note that, despite the apparent similarity in the appearance of orbital **I** in **1** and **2**, the difference in the amount of π-delocalization between diarylphosphenium and diaminophosphenium cations is also clearly manifested in the metrical parameters, both calculated and experimentally determined, of such species. For example, the P−N bond lengths of diaminophosphenium cations that have been characterized in the solid state are intermediate between single bonds (1.800(4) Å for O_3PNH_3)[41] and double bonds (1.495(4) for 2,4,6-tri-^{t}butylphenyl-N═PCl),[42] as one would expect for a molecule that contains a delocalized π-system. The P−N distance calculated for **2** is 1.6402 Å and falls in the range of those determined experimentally (1.58−1.69 Å),[15] and the P−N bond has a bond order of 1.5, as determined by the NBO analysis. In contrast, the calculated P−C_{ipso} bond length of 1.7604 Å in Ph_2P^+ is consistent with P−C single-bond lengths found in the Cambridge Structural Database (CSD)[43] and has an NBO bond order of 1, emphasizing limited π delocalization.

Overall, it is evident from the examination of the electronic structure of the two types of phosphenium cations that diphenylphosphenium cations should be better acceptors than their diaminophosphenium analogues. Despite this observation, several adducts of diaminophosphenium cations have been reported;[15] thus, we undertook a series of calculations to determine the energetic and structural consequences attributable to the nature of the substituent groups in phosphenium acceptor complexes.

3.2. Acceptor Complexes. 3.2.1. Reaction Energies and Energy Decomposition Analysis. To elucidate the acceptor properties of phosphenium cations **1** and **2**, we performed calculations on models of acceptor complexes formed between the cations and three different types of donors that have been studied experimentally. The model donors that were chosen are as follows: trimethylphosphine (as a model for phosphine donors), para-aminopyridine (DHAP, as a model for para-(dimethylamino)pyridine (DMAP) and pyridine donors), and imidazol-2-ylidene (NHC, as a model for *N*-heterocyclic carbene donors). Pertinent calculated data concerning the donor molecules are compiled in Table 2,

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Table 3. Calculated Energies for Adducts to **1** and **2**

model	symmetry	corrected energy, E_{total}^{a} (au)	cation ΔH_{prep}^{b} (kJ/mol)	P−E bond energy^{c} (kJ/mol)	ΔH_{rxn}^{d} (kJ/mol)
3-Ph	C_1	−1265.18877	39.1	295.7	−220.7
3-NMe$_2$	C_s	−1071.08756	134.0	251.7	−91.2
4-Ph	C_1	−1107.74284	46.4	283.0	−217.7
4-NMe$_2$	C_1	−913.65060	67.2	194.5	−111.8
5-Ph	C_1	−1030.34756	47.7	375.0	−308.5
5-NMe$_2$	C_s	−836.25143	165.0	374.6	−192.3

[a] $E_{total} = E_{calculated} + 0.9774(\text{ZPVE})$. [b] The preparation energy for the caton is calculated for the process "acceptor → acceptor*"; $\Delta H_{prep} = E_{acceptor*} - E_{acceptor}$, where the asterisk (*) indicates that the acceptor fragment is in the exact same geometry observed in the coordination complex. [c] The phosphorus−element (P−E) bond energy is calculated by "complex → donor* + acceptor*"; the bond energy (BE) is given as BE = $(E_{donor*} + E_{acceptor*}) - E_{complex}$. [d] For the reaction "donor + acceptor → complex", $\Delta H_{rxn} = E_{complex} - (E_{donor} + E_{acceptor})$.

and important calculated energies for the model complexes are listed in Table 3; depictions of the optimized geometries of the donors, acceptors, and complexes are presented in Figure 2.

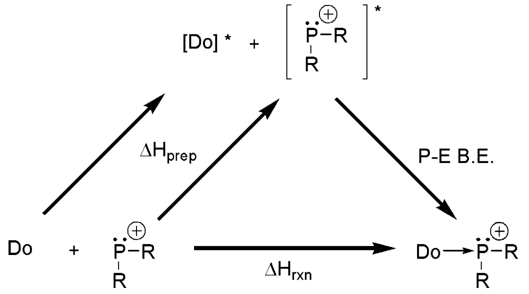
Several quantities that allow for the assessment of the electron-donating ability of each of the donor molecules are listed in Table 2. Although the calculated absolute hardness (η) values for each of the molecules are virtually identical, the proton affinity (PA), pK_a, and absolute electronegativity (χ) values suggest that (i) DHAP might be a slightly better donor than PMe$_3$ and (ii) the NHC complex is significantly more basic than both of the other molecules. The relative energies of the highest occupied molecular orbitals (HOMOs) also indicate that NHC is the most effective donor; however, these values suggest that donation from PMe$_3$ should be more favorable than donation from DHAP. The consequences of the differing donor abilities of these molecules, in regard to the formation and structural features of donor−acceptor complexes, are discussed later in this work.

One of the most instructive quantities that we determined for these model systems is the reaction energy of complex formation, because it provides a measure of the thermodynamic favorability for donor−acceptor complexes over the free acid and base. Complex formation is found to be exothermic in all cases. For a given donor molecule, the reaction energies for complex formation are always significantly more exothermic for complexes of diphenyl phosphenium cations than those for the diamino analogues. This observation is in agreement with the predictions based on the electronic structure of the phosphenium cations outlined previously and confirms that diphenylphosphenium cations are better acceptors than diaminophosphenium species are.

As one would predict on the basis of the PA or pK_a values, for a given phosphenium cation, the reaction with the carbene model is significantly more exothermic (by ~100 kJ/mol) than are the reactions with either of the other donors. The reaction energies for the formation of complexes with PMe$_3$ and DHAP with a given cation are comparable to each other, with the phosphine being slightly more exothermic in the complex with **1** and the pyridine being more favorable in the complex with **2**.

A Ziegler-type Generalized Transition State Analysis[47] of the donor and acceptor fragments has been performed to gain insight into the differences between the reaction energies of adduct formation and the strengths of the donor acceptor bonds; the approach to the energy decomposition analysis is illustrated in Scheme 4. In regard to the reaction energies, the most important difference between systems involving cations **1** and **2** is found in the preparation energies (ΔH_{prep}) for the cations (note that the preparation energies for the donors do not vary significantly from one complex to the other and are minor in the case of the NHC and DHAP donors). The preparation energy provides a measure of the energy required to distort a given molecule or ion from its most stable structure to the geometry that is observed in the complex. From the data in Table 3, two important observations regarding ΔH_{prep} of the acceptors can be made. First, the magnitude of ΔH_{prep} of **1*** remains virtually constant (40−50 kJ/mol), regardless of the nature of the donor molecule. Second, the amount of energy required to distort the diaminophosphenium cation is always significantly greater than that required for the diphenyl analogues. The greater preparation energy requirement for **2*** is a direct consequence of the greater π delocalization in **2** in the sense that the breaking of the π-system on the diaminophosphenium cation is necessary to allow for all of the subsequent distortions.

Scheme 4. Energy Decomposition Analysis Scheme for the Complexation Reaction of a Donor (Do) to a Phosphenium Cation, Where ΔH_{rxn} is the Reaction Energy, the Two ΔH_{prep} Terms are the Energies Required to Distort the Donor and Acceptor to the Geometries Observed in the Complex (Indicated by Asterisks), and BE Is the Energy of the Phosphorus−Element (P−E) Bond in the Complex.



In the case of the carbene adducts **5-Ph** and **5-NMe$_2$**, the entire difference between the respective reaction energies can be attributed to the differences in the preparation energies of the acceptor cations. It seems as if the strong NHC donor provides sufficient electron density to the vacant 3p orbital to remove the π delocalization in **2** completely and causes the most distortion, whereas the weaker bases do not have such a large effect. For the other complexes, the differences in ΔH_{prep} of the cations make a significant but lesser

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(47) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1−10.

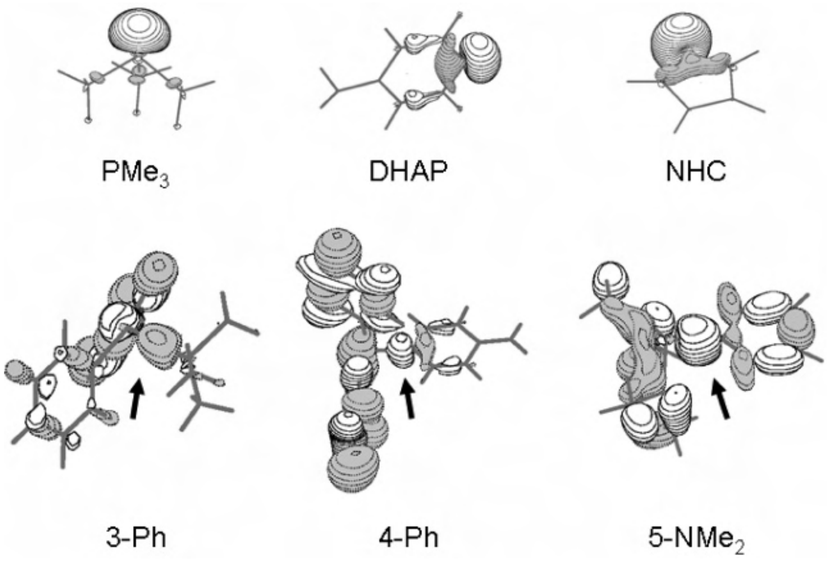

Figure 5. Top row, "lone pair" MO of the donor molecules; bottom row, selected MOs showing the fate of the donor lone pair MOs after complexation. The lobe attributable to the lone pair in each MO is indicated by an arrow.

contribution to ΔH_{rxn}. In the case of **3-NMe$_2$**, the relatively large value of ΔH_{prep} is likely a consequence of the steric requirements of the PMe_3 donor. Although the steric requirements of the other donor ligands could likewise influence the magnitudes of ΔH_{prep} of the cations, the size and shape of the model DHAP and NHC donors are essentially identical; thus, the differences in the calculated enthalpies seem to be more related to donor ability.

Given the large differences in reaction energies, it was surprising to find that the energies of the donor−acceptor bonds are remarkably similar for both adducts of a particular donor molecule. The NHC adducts have identical P−C bond energies of ~375 kJ/mol, which is significantly larger than the typical P−C single-bond energy of ~264 kJ/mol.[48] There are somewhat larger differences between the bond energies of each of the PMe_3 adducts and the DHAP adducts; however, the energies do fall in the range typical of P−P (209−239 kJ/mol)[48,49] and P−N single bonds (279−331 kJ/mol),[50,51] with the exception of **4-NMe$_2$**. The strength of the donor−acceptor bonds that are formed attest to the viability of coordination chemistry as a general method for P−E bond formation.

The shapes of the molecular orbitals in complexes **3-Ph** to **5-NMe$_2$** provide qualitative insight into the nature of the donor−acceptor interactions and seem to be related to the electronegativity of the donor atom. The orbitals depicted in Figure 5 are those that result primarily from the in-phase combination of the $3p_\pi$ orbital on the phosphenium acceptor and the "lone pair" orbital on the donor molecule (illustrated above the MO from a corresponding donor−acceptor complex for comparison). The lobe corresponding to the lone pair on the DHAP fragment in **4-Ph** seems almost identical to that of the free DHAP ligand, which seems to be the weakest donor in this series and remains localized on the N atom (as one would expect on the basis of electronegativity for a polar bond). In contrast, the lone pair lobe from the NHC fragment in **5-NMe$_2$** is considerably distorted from its original shape and the resultant lobe is distributed evenly between the P and C atoms, as one would expect for a nonpolar covalent bond. The lone pair lobe in **3-Ph** has an appearance that is intermediate between those of the DHAP and NHC ligands.

The conclusions regarding the nature of the donor−acceptor interactions based on the fate of the lone pair orbitals in the MOs of the complex are supported by the analysis of the Laplacians of the electron density, $\nabla^2\rho$. Figure 6 shows contour maps of $\nabla^2\rho$ calculated in the E−P−R plane for each of the donor-$P(NMe_2)_2^+$ complexes; contour maps of $\nabla^2\rho$ for the donor-PPh_2^+ complexes exhibit similar features and are included in the Supporting Information. Examination of the contour maps reveals significant differences in the nature of the donor−acceptor bonds in the three complexes. In complexes **3-NMe$_2$** and **5-NMe$_2$**, there are significant regions of local electron density concentration (indicated by the solid contour lines) between the donor atoms and the P atoms. In fact, the appearance of each of these regions of electron density concentration resembles those in the region between the P atom and the N atom of the covalently bonded NMe_2 substituent. In stark contrast, the region between the N atom of the DHAP ligand and the P atom in the $\nabla^2\rho$ map of **4-NMe$_2$** shows virtually no shared concentration of electron density. The electron density associated with the lone pair of the DHAP donor remains localized on the N atom and, thus, the donor−acceptor interaction in **4-NMe$_2$** seems to be significantly more ionic than those in **3-NMe$_2$** or **5-NMe$_2$**. Overall, the mixture of covalent and ionic features in the electron density distribution of **4-NMe$_2$**

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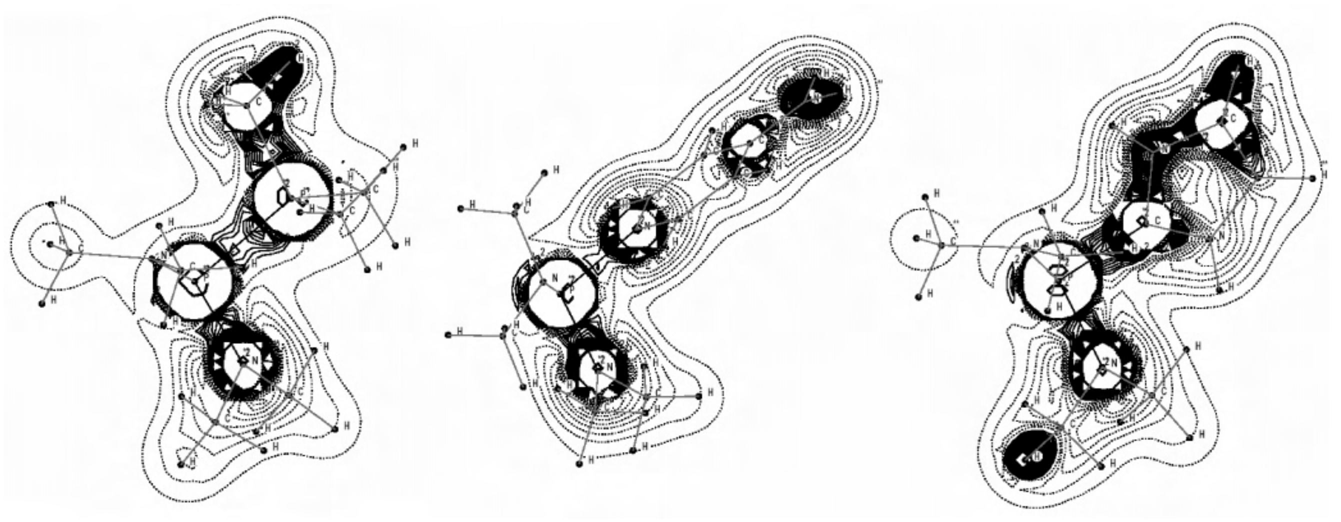

Figure 6. Contour maps of the Laplacians of the electron density for complexes **3-NMe₂**, **4-NMe₂**, and **5-NMe₂** calculated in the R−P−E plane. Regions of locally concentrated electron density are indicated by solid contours and regions of locally depleted electron density are indicated with dotted contours.

Table 4. Calculated Electronic Properties for Adducts to **1** and **2**

model	q(P)[a] (au)	E_{HOMO} (eV)	E_{LP}[b] (eV)	LP population[c]	proton affinity, PA[d] (kJ/mol)	Δq(P)[e] (au)
3-Ph	0.69	−10.08	−10.08	1.911	−588.1	0.40
3-NMe$_2$	1.05	−9.95	−10.37	1.915	−572.1	0.42
4-Ph	1.09	−9.77	−9.77	1.938	−631.1	0.49
4-NMe$_2$	1.40	−9.56	−9.56	1.964	−617.6	0.57
5-Ph	0.96	−10.03	−10.03	1.874	−592.1	0.43
5-NMe$_2$	1.27	−9.98	−10.58	1.888	−578.1	0.48

[a] Natural bond order (NBO) charge on the phosphenium P atom in the complex. [b] Energy of the "lone pair" orbital localized on the P atom in the complex. [c] NBO population of the lone pair on the P atom. [d] Proton affinity for protonation of the P atom in the complex. [e] Change in NBO charge on the former phosphenium P atom in the complex after protonation.

appears remarkably similar to that which was calculated for the model P$^{\mathrm{V}}$ cation $[(H_3N)_2P({=}NMe)_2]^+$.[52]

Several electronic properties of the model coordination complexes, listed in Table 4, were calculated in an attempt to gain further insight into the nature of the donor−acceptor interaction. Although there is no obvious relationship between any of these values and the strength of the donor−acceptor interaction (as measured by either the P−E bond energy or ΔH_{rxn}), there are some features that are worthy of mention. First, despite the relatively small changes in the charge on the phosphenium P atoms upon coordination of Lewis bases, the lone pair orbital on the P atoms are significantly destabilized upon formation of the complexes. This destabilization, with respect to the corresponding orbitals in **1** and **2**, is manifested not only in the energies of the orbitals but also in the PAs of the complexes. Although it is evident that donor coordination of phosphenium cations enhances the basicity of phosphenium cations, the lack of a simple relationship between the strength of the donor and the magnitude of the change is consistent with the conclusions of Howard et al., regarding the nature of substituent effects on the basicity of group 15 bases.[53]

3.2.2. Donor−Acceptor Complex Structural Features. The calculated geometrical features of the donor−phosphenium cation complexes provide values that may be compared to experimental observations to assess the accuracy of the computations. In addition, the metrical parameters provide significant insight into the nature of the bonding and complement the energetic and electronic analyses outlined in the previous section. Important calculated structural features are compiled in Table 5, and a selection of metrical parameters from pertinent reported compounds are listed for comparison.

As shown by the data in Table 5, the lengths of the P−donor atom bonds and the other metrical parameters are modeled well by our calculations (taking into account the differences between the model systems and the real systems and the differences between the gas phase at 0 K and the solid state at ambient temperature). For example, the calculated P−N$_{\mathrm{substituent}}$ distances are in the range of 1.665−1.725 Å and are consistent with the experimental distances shown in Table 5. Similarly, the computed P−C$_{\mathrm{substituent}}$ bond lengths of 1.824−1.838 Å are typical of those that one would expect for a phosphorus−phenyl linkage. Furthermore, the lengths of the donor−acceptor bonds are all typical of P−E single bonds (e.g., the P−P distance is 2.212(1) Å for Me$_2$-PPMe$_2$),[56] although there are some features to note. The length of the bond between DHAP and the P atom is

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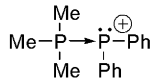
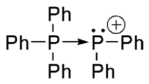
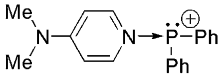
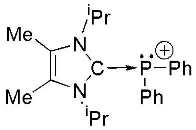
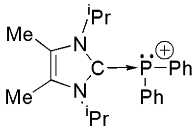
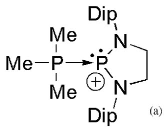
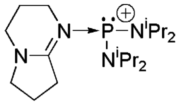
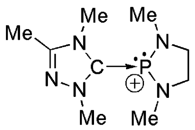
Table 5. Selected Calculated or Experimentally Determined Metrical Parameters for Model Complexes **3**−**5** and Comparable Reported Phosphenium Complexes[a]

Cation	Anion	P-R	P-E	R-P-R	R-P-E	Ref.
	[OTf]	1.816(6) 1.833(6)	2.187(2)	107.9(3)	100.86(18) 101.33(18)	39
	[OTf]	1.831(3) 1.838(3)	2.221(1)	102.78(12)	102.28(9) 106.55(9)	39,54
3-Ph	Calc'd	1.832 1.836	2.224	109.1	100.2 101.0	This Work
	[OTf]	1.81(1) 1.80(1)	1.78(1)	104.0(7)	99.3(6) 104.4(6)	38
4-Ph	Calc'd	1.824 1.825	1.858	105.7	99.5 99.7	This Work
	[$AlCl_4$]	1.810(8) 1.827(8)	1.813(7)	106.5(3)	101.3(3) 102.3(3)	55
	[$GaCl_4$]	1.830(20) 1.833(20)	1.828(20)	106.2(9)	100.6(10) 104.0(10)	This Work
5-Ph	Calc'd	1.829 1.838	1.844	108.1	97.7 99.7	This Work
	[OTf]	1.661(2) 1.696(2)	2.3065(9)	92.3(1)	99.74(8) 109.13(8)	7
3-NMe$_2$	Calc'd	1.691 1.691	2.253	115.6	100.5 100.5	This Work
	[PF_6]	1.661(4) 1.666(4)	1.796(3)	109.4(2)	99.0(2) 101.6(2)	12
4-NMe$_2$	Calc'd	1.665 1.725	1.925	101.9	93.2 104.2	This Work
	Calc'd	1.717 1.718	1.910	95.8	95.9 102.1	21
5-NMe$_2$	Calc'd	1.705 1.705	1.844	117.9	96.3 96.3	This Work

[a] Bond lengths given in angstroms, bond angles given in degrees. Note that, for the diphenylphosphenium adducts, R = C; for diaminophosphenium adducts, R = N; and for PMe_3, DHAP, and NHC adducts, E = P, N, and C, respectively. [b] Dip = 2,6-di-isopropylphenyl.

considerably different when the substituent is phenyl (1.858 Å in **4-Ph**) than when the substituent is dimethylamido (1.925 Å in **4-NMe$_2$**). Such variation is consistent with the weaker calculated bond energy in **4-NMe$_2$** and is suggestive of competitive electron donation to the P atom from the lone pair of the amido substituent with a planar geometry at a distance of 1.665 Å. The distances in complexes **3-Ph** and **3-NMe$_2$** are consistent with a bonding situation intermediate

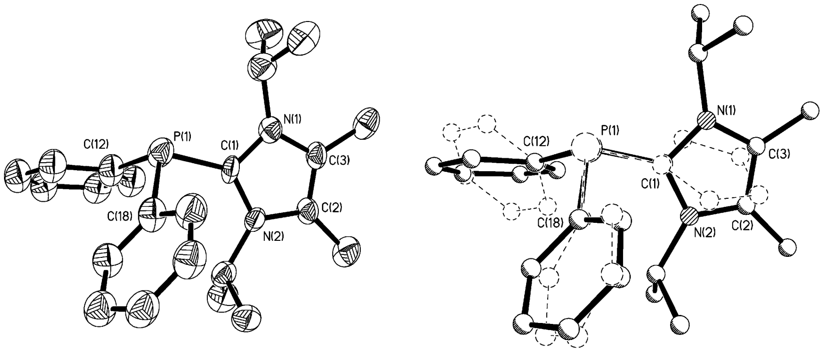
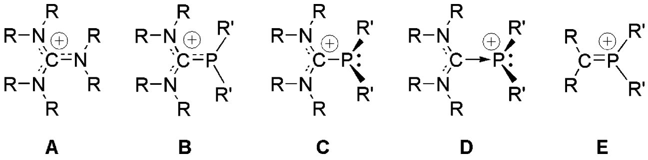


Figure 7. Left: Solid-state structure of the cation in **6**[$GaCl_4$]. Ellipsoids are 30% probability, one (of two) crystallographically distinct molecules is shown; two C_6H_6 solvate molecules, the anions, and the H atoms have been removed, for clarity. Right: Comparison of the structures of the real cation **6** (solid structure) and the model cation **5-Ph** (dashed structure).

Scheme 5. Canonical Structures Showing a Typical “Planar” Guanidinium Cation (A), Possible Structures for a Mono-phosphaguanidinium Cation (B and C), the Donor−Acceptor Complex (D), and a Methylenephosphonium Cation (E).

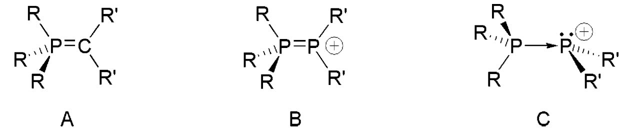


between those of the other donors. For the strongest donor (NHC), the length of the donor−acceptor bond (1.844 Å) seems to be virtually unaffected by the type of substituent present on the P center. Further evidence that the strong donation of the NHC completely disrupts the N−P−N π-system in **5-NMe₂** is provided by the strongly pyramidalized N atoms in the dimethylamido substituents; although no experimental analogue exists for **5-NMe₂**, the calculated structure in Table 5 exhibits similar pyramidalized N atoms adjacent to the P atom.[21]

The solid-state structure of the real salt [$Ph_2P{-}NHC'$]-[$GaCl_4$] (**6**[$GaCl_4$]) is shown in Figure 7 and demonstrates that the calculations accurately predict the C−P connectivity from the imidizole-2-ylidene ligand on diphenylphosphenium. As shown in Figure 7, the $P{-}C_{donor}$ distance of 1.853(2) Å and other metrical parameters deviate only slightly from the calculated values; the only major differences are in the torsion angles, and these variations are attributable to the simplifications used in the model system. The metrical parameters of **6**[$GaCl_4$] compare well to the previously reported $AlCl_4^-$ derivative.[55]

The most notable structural feature in each of the complex structures, as clearly shown in Figure 7, is the pyramidal P atom from the phosphenium fragment. This geometrical feature is exhibited regardless of the nature of the substituents on the P atom (at least those that we have examined) and it highlights the difference between the donor−acceptor complexes studied in this work and related molecules typical of organic chemistry. For example, the structures of **5-Ph** or the real cation [$Ph_2P{-}NHC'$]$^+$ are clearly not analogous to those of the “planar” guanidinium cations (Scheme 5);[57] the putative structure, which has a planar geometry about the P atom, is >120 kJ/mol higher in energy than the fully optimized structure and it is not a minimum on the potential energy surface.[40] Although such behavior is often attributed simply to the higher planarization energy of phosphorus, with respect to that of nitrogen, the existence of stable methylenephosphonium ([$R_2P{=}CR'_2$]$^+$)[58] salts that exhibit trigonal planar phosphorus environments suggests that the overall structure of **5-Ph** is probably more accurately considered as one of the most extreme examples of the distortion of a potential multiple bond in terms of the Carter−Goddard−Malrieu−Trinquier (CGMT) model.[59] Instead of having a C−P multiple bond, or even a distorted bis-donor−acceptor bond (typical of heavier carbene analogues), the bonding in **5-Ph** is best described as having the NHC fragment acting purely as a donor and the phosphenium fragment behaving exclusively as an acceptor (**D** in Scheme 5). Such a situation arises because of the strong preference of the singlet state for both the NHC and the phosphenium cation ($\Delta E_{s\rightarrow t} = 127$ kJ/mol for **1** and 193 kJ/mol for **2**);[40] the electronic preference of the system enforces the pyramidal geometry at phosphorus and leaves a stereochemically active “lone pair” of electrons on the P atom. In this context, coordination of a carbene with a much smaller singlet−triplet energy difference (or with a triplet ground state) should result in the formation of cations with structures such as that of **E** depicted in Scheme 5.

Scheme 6. Canonical Structures Illustrating the Geometry Adopted by (A) a Typical Wittig Reagent, (B) the Unfavorable Phospha-Wittig Structure (B), and (C) the Most-Stable Structural Isomer.



In a similar vein, the pyramidal phosphorus center in **3-Ph** does not conform to the geometry expected for a Wittig reagent analogue. Virtually all of the structures of Wittig reagents collected in the CSD exhibit a trigonal planar geometry at the carbenic center (**A** in Scheme 6), in stark contrast to the pyramidal geometry in the calculated and experimentally observed [$R_3P{-}PR'_2$]$^+$ complexes. We have

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found that the putative trigonal planar phosphenium−PMe_3 complexes (**B** in Scheme 6) are more than 90 kJ/mol higher in energy than are the pyramidal structures observed experimentally. In fact, such geometries are not true minima on the potential energy surface, having a single imaginary frequency that corresponds to the pyramidalization of the P environment.[40] The reason for the different structural preferences between the carbon and phosphorus analogues is again attributable to CGMT theory and the relative stabilities of the singlet and triplet ground states. The singlet state of a phosphenium cation, even if it bears weak π-donor substituents, is significantly more favored than the singlet state of diphenylcarbene.[18] The overwhelming preference for singlet behavior in **1** and **2** precludes the adoption of a traditional Wittig-type geometry.

4. Conclusions

Calculations on related free phosphenium cations show that Ph_2P^+ is a better Lewis acid, relative to a diaminophosphenium analogue, despite the greater positive charge on the P atom of the latter cation. The differing acidity is largely attributable to the ineffective delocalization of the phenyl π-system with the empty p-orbital on the P atom and is reflected in a lower-energy LUMO. The effects of differing substitution have been quantified, especially in terms of the energies of the frontier orbitals. Furthermore, the lack of an effectively delocalized π-system on **1** results in lower preparation energies for the cation, in comparison to **2**, required for adduct formation with neutral Lewis bases and, thus, renders adduct formation even more energetically favorable.

Although the nature of donor−acceptor interaction is dependent on the composition of the donor molecule, the bond energies calculated for the donor−acceptor bonds formed are comparable to or greater than the energies reported for covalent phosphorus−element (P−E) bonds. The strength of these bonds attests to the viability of coordination chemistry as a general method for P−E bond formation and to the synthetic utility of the Ph_2P^+ fragment. Furthermore, the basicity of both types of phosphenium cations is significantly enhanced by donor complexation, which may be of significant experimental utility.

The structural features of the calculated donor−acceptor complexes are in excellent agreement with related examples that have been observed experimentally. The structures of the phosphenium cation complexes with *N*-heterocyclic carbene and trimethylphoshine do not resemble those of typical guanidinium cations or Wittig reagents, respectively. The preference for donor−acceptor complexes, in lieu of multiple-bonded alternatives, is understood, in terms of the Carter−Goddard−Malrieu−Trinquier (CGMT) approach.

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Supporting Information Available: Summary of computational results and crystallographic data (PDF and CIF). This information is available free of charge via the Internet at http://pubs.acs.org.

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