J. Phys. Chem. A **1999,** *103,* 10998−11003

A DFT/Electron Localization Function (ELF) Study of the Bonding of Phosphinidenes with N-Heterocyclic Carbenes

Gilles Frison* and Alain Sevin

Laboratoire de Chimie Théorique, UMR 7616 Université Pierre et Marie Curie and CNRS, Case courrier 137, 4 Place Jussieu, 75252 Paris Cedex 05, France

Received: May 11, 1999; In Final Form: September 21, 1999

The bonding between model phosphinidene PH and two types of cyclic Arduengo's carbenes, the aromatic $C_3H_4N_2$ (**1**) and the related saturated $C_3H_6N_2$ (**2**) species, respectively, have been analyzed in terms of the electron localization function (ELF). In a first step, the bare carbenes have been studied, and then, in a second step, the changes brought about by PH complexation have been treated. It has been shown that the bonding mode essentially results from a dative bond formed by the nucleophilic carbenic carbon of the ring and the PH acceptor site. Some back bonding from P creates a partial double-bond character around the C−P unit. The latter character is more pronounced when PH is linked to the saturated carbene **2**. A comparison of the ring aromatic properties, in terms of nucleus-independent chemical shifts has been achieved, showing that complexation of **1** by PH diminishes the ring aromaticity through relocalization of the electrons on the N atoms.

Introduction

The isolation of stable N-heterocyclic carbenes, of either type **1** or **2** (Figure 1), by Arduengo and co-workers[1,2] has initiated a vast series of both experimental and theoretical new investigations. It has been shown that the presence of bulky R substituents is necessary for stabilizing free species, mostly by steric inhibition. A great variety of less heavily substituted carbenes, coordinated to ligands such as molecules containing main group atoms, rare-earth, and transition-metal complexes have been characterized.[1] In **1** or **2**, the ground state (GS) electronic configuration is singlet, with a singlet−triplet gap around 85 kcal mol^{-1}.[3] In **2**, the gap is smaller due to the inhibition of the 5-center 6-electron π-delocalization that strongly stabilizes the singlet GS of **1**.[4] It has been shown that, in contrast with two oxygen atoms, the presence of two N or S atoms affords an important stabilization to the 6π-electron system.[5] An interesting proposal stating that the stabilization of cyclic species mostly comes from the σ-skeleton,[6] has been ruled out by theoretical studies.[7,8] With CH_2 as a reference compound, the isodesmic balances calculated for the conformers of **3** displayed in the right part of Figure 1 show the following: (i) the σ-type stabilization of **3** ⊥ where no π-type conjugation is present amounts to about 20 kcal mol^{-1}; (ii) in the planar geometry, **3** //, the π-donation from the N lone pairs is about 70 kcal mol^{-1}; (iii) the $CH_2{-}CH_2$ bridging increases the overall stabilization by only 6 kcal mol^{-1}; and (iv) the unsaturated bridging linkage $CH{=}CH$ yields an additional stability of 26 kcal mol^{-1} to the preceding one. Two important conclusions can then be drawn. The first one is that most of the stabilization comes from donation of the N lone pairs to the empty π orbital located on the carbenic C atom. The second one is that **1**, which is more stable than **2** by around 20 kcal mol^{-1}, bears some aromatic character.

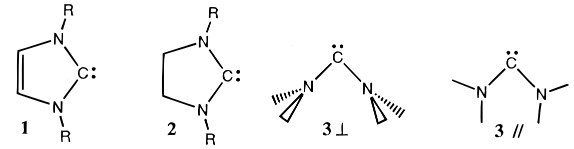

Figure 1. Structural features of **1**−**3**. See Figure 3 for detailed geometries.

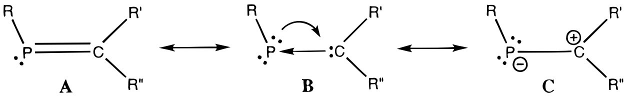

Figure 2. Limiting resonance structures involved in a double P−C bond.

In many experimental studies, N-heterocyclic carbenes are associated with a large series of complexing ligands. Among complexing ligands, unsaturated phosphinidenes, RP, are particularly interesting. With aliphatic carbenes, the RP bonding with carbenic carbons remains ambiguous and might be regarded as intermediate between the limiting resonance structures displayed in Figure 2. In structure A, we have a true P═C double bond, yielding a classical phosphaalkene molecule, whereas in structure C, we have an ionic P−C bond. In structure B, the bonding is more complex: the carbene provides its lone pair to P in a dative fashion, whereas back bonding from a lone pair of P, toward the empty π-type MO of the carbene, yields some double-bond character to the PC linkage.[9−16] The same dichotomy has been observed when dealing with Arduengo's carbenes bound to PR species.[17−21] A similar ambiguity has been found in Ti, Zr, and Cr complexes of phosphinidenes. In the latter cases, theoretical studies have shown that the actual electrophilic or nucleophilic behavior of the PR ligand depends on a complex balance between σ-bonding and π-back-bonding, but it is noteworthy that, this time, PR acts as an electron donor, whereas the back-bonding arises from the metal MO's.[22] We thus see that PR moieties may act as σ-electron donors and π-electron acceptors when linked to transition-metal complexes as well as σ-electron acceptors and π-electron donors when linked to carbene species. In all cases, quantum mechanical calculations yield delocalized wave functions, whose resulting overall electronic charges or densities are very difficult to analyze in terms of localized electronic structures. To overcome this intrinsic difficulty, we propose here an electron localization function (ELF) study of the various *localized* contributions in

10.1021/jp991550q CCC: \$18.00

TABLE 1: Calculated Energies of PC Bond in Compounds 5 and 6 by Various Methods

energy of the PC bond[a]	MP2 6-31G*	B3LYP 6-31G*	B3LYP 6-311+G(2df,p)	CCSD(T)[b] 6-31G*
5	59.16	62.69	60.51	55.28
6	69.10	69.27	66.56	64.19

[a] Without ZPE correction. [b] B3LYP/6-31G* geometry.

isolated N-heterocyclic carbenes of **1** and **2** types, either free or linked to PR molecules. For the sake of comparison, some related cyclic or open chain compounds will be examined with the same method.

Methodology

All calculations have been carried out with the Gaussian 94 series of programs.[23] The calculations were first achieved on compounds **1**, **2**, **5**−**7**, and **7t** at various levels of basis set and correlation: DFT/B3LYP[24]/6-31G*,[25] MP2/6-31G*, DFT/B3LYP/6-311+G(2df,p), and CCSD(T)/6-31G*//DFT/B3LYP/6-31G*. There are only very little differences (maximum deviation 0.02 Å and 1°) between all of the geometries optimized with these methods. Upon comparison of the C−P bond energies (Table 1), with triplet PH as a reference, one sees that comparable results are obtained for **5** and **6**. It is noteworthy that using the same DFT technique, the limited 6-31G* basis set affords results that remain very close to these obtained with the more extended 6-311+G(2df,p) basis set. Accordingly we kept the B3LYP/6-31G* method, which allows short computing times for our systematic study of the compounds displayed in Figure 3 and Table 2, as well as for more substituted compounds not described in this report. All structures have been fully optimized, with the exception of compounds **3** ⊥, **3** ⊥ **t**, and **4** ⊥ for which geometry constraints were imposed; each CNH_2 unit was fixed in a planar geometry perpendicular to the N−C−N plane, and for compound **4** //, each NH_2 unit was fixed in a planar geometry. (Upon relaxation of the constraint upon CNH_2 planarity in the case of **3** ⊥**,** one obtains two local energy minima, with the least stable having a NCN angle of 106.9° and a NC bond length of 1.450 Å with both NH_2 pyramidalyzed. A second local energy minimum having a D_{2h} linear geometry was found 19.5 $kcal.mol^{-1}$ below. With the constraints imposed to **3** ⊥, a stable triplet state, labeled **3** ⊥ **t** was also found; see Figure 3 and Table 2.) It is noteworthy that when dealing with **4**-type compounds, the actual optimal geometry is the nonplanar structure **4** (C_1 geometry; see Figure 3). A vibrational analysis was done at the same level of calculation to characterize stationary and criticals points (see Table 2) and thereby to estimate their zero-point vibrational energies (ZPEs) whose calculated values were scaled by 0.98.[26] Reed and Weinhold's NBO analysis[27] of **1**−**6** gave the π population and orbital hybridizations. The geometries are displayed in Figure 3, and the corresponding ZPE-corrected energies are given in Table 2. ELF calculations were achieved using the wfn output of B3LYP runs, using the TopMod series of programs written in our group[28] (more detail on ELF is given elsewhere[29−31]).

The aromatic character of **1** and **5** was evaluated by computing the nucleus-independent chemical shift (NICS, GIAO−SCF/6-31+G*//B3LYP/6-31G*) and compared to that of benzene, calculated with the same technique, for two typical points, with the first one located at the center of the five-membered ring and the second one 0.5 Å above.[32]

Structural and Thermochemical Analysis of the CP Linkage in Compounds 1−9

Free Carbene Species 1−3. The strong interaction of the N lone pair with the adjacent carbene-type carbon atom, labeled C_c for convenience in the coming discussion, has already been emphasized in the Introduction (vide supra). Accordingly, we will only briefly discuss the calculated results displayed in Figure 3, keeping in mind that they provide a basis for further analysis of the CP bonding. The influence of N donation toward C_c is clearly illustrated by the comparison of the CN bond length in **3** // and **3** ⊥. In **3** //, a C_cN bond length of 1.344 Å, intermediate between the standard value of a true CN double bond (1.250 Å in formaldimine), and that of a CN single bond (1.453 Å in methylamine), calculated with the same basis set is obtained.[33] In **1**, the bond lengths between heavy atoms are almost equal, in agreement with the aforementioned aromatic character. The delocalization of the N lone pairs on the three carbon centers renders the donation from both N atoms to C_c less pronounced; thus, a C_cN bond length (1.372 Å) longer than that in **3** // (1.344 Å) is actually found. As expected, the C_cN partial double-bond character (1.354 Å) is more important in **2** than it is in **1**. It is noteworthy that a weak distortion from planarity is observed in **2**, yielding a C_2 geometry, with NCNC and NCNH dihedral angles, respectively, of 5.8° and 165.6°. This shows that NC conjugation competes to some extent with the torsional repulsion arising with the quasieclipsed CH_2 ring units.

CP Linkage in Compounds 4−9. First of all, it is noteworthy that in these species, the PH bond length remains practically constant and does not deserve special comment. Structures **8** and **9** provide models, respectively, for a single (1.876 Å) and a double CP (1.674 Å) bond. Keeping these values in mind, the comparison of **4 //** and **4** ⊥ leads to a paradoxical conclusion, because the apparently more conjugated moiety, **4** //, has a longer C_cP bond (1.762 Å) than that of its counterpart in **4** ⊥ (1.696 Å) in which conjugation is absent. In the latter compound, the bond length is close to that of **9** (1.674 Å), and it is clear that the only driving force leading to a pronounced double-bond character consists of a transfer of electronic density from the P lone pair(s) to the electrophilic π-type MO located on C_c. We thus arrive at an important finding: (i) the double-bond character results from P-electron donation to C_c; (ii) when N-electron donation to C_c competes with P-electron donation to the same center, the double-bond character of C_cP decreases. These fundamental trends are confirmed by examination of **5**, in which the C_cP bond length is 1.763 Å, at practically the same value as that in **4** // (1.762 Å). In **6**, the structural distortions from planarity are even more pronounced than those in **2**, in such a way that the maximum extension direction of the N lone pairs prevents them from efficiently overlapping with the empty π-type MO located on C_c. With respect to the bond lengths of **5**, **6** has a slightly longer C_cN bond (1.381 Å instead of 1.378 Å) and a shorter C_cP bond (1.745 Å instead of 1.763 Å). We thus reach the same conclusion as when dealing with **4** // and **4** ⊥ (vide supra): the partial double-bond character is more present in **6** than in **5**, because the double-bond character is less compensated by N contributions. It is noteworthy that in actually available structural data, the distortion from planarity is much more pronounced than in our model compounds, due to the presence of aliphatic or aromatic substituents on N or P atoms. The last point would render a comparison of our calculated results with available XR data[18−20] rather formal. (A study of these compounds, complexed by various PX (X = H, CH_3, CF_3), is in progress in our group.)

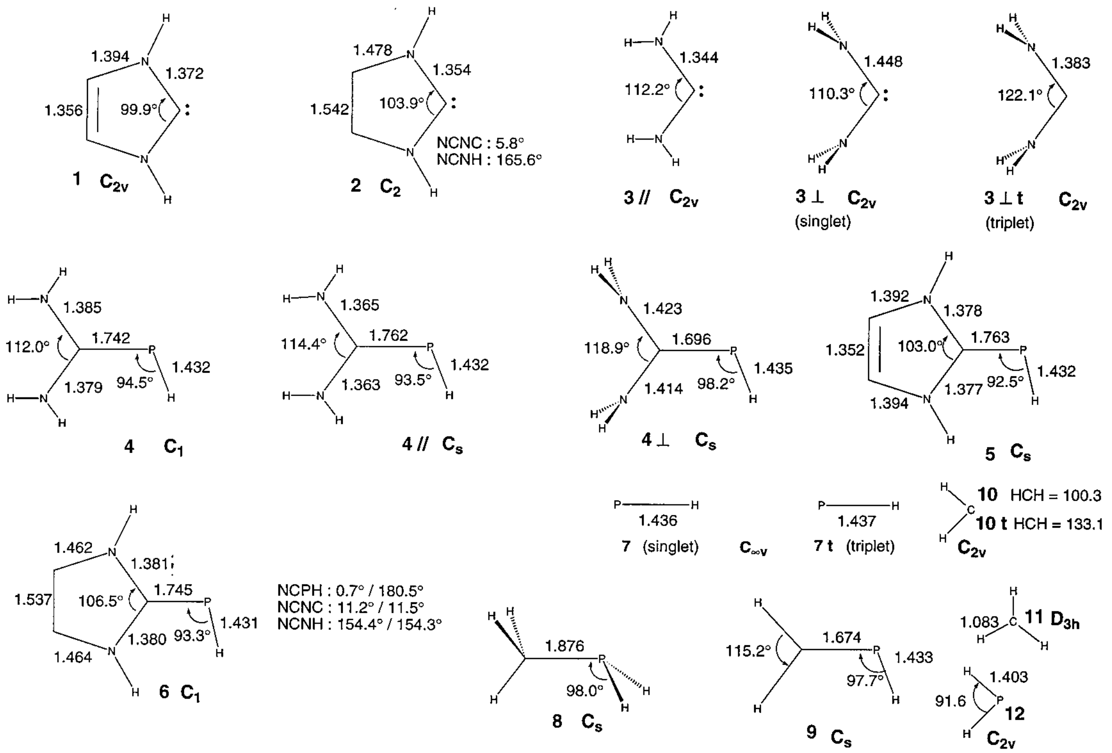

Figure 3. Principal structural parameters for **1**−**12**.

TABLE 2: Calculated ZPE-Corrected Energies and Number of Negative Eigenvalues of 1−12[a]

compounds	energy (au) ZPE corrected	negative eigenvalues
1	−226.096 798	0
2	−227.279 494	0
3 //	−149.901 243	0
3 ⊥	−149.756 577	4
3 ⊥ t	−149.810 074	3
4	−491.875 899	0
4 //	−491.874 111	2
4 ⊥	−491.826 380	4
5	−568.063 825	0
6	−569.255 220	0
7	−341.818 606	0
7 t	−341.871 933	0
8	−382.404 042	0
9	−381.186 291	0
10	−39.111 996	0
10 t	−39.132 954	0
11	−39.809 059	0
12	−342.491 016	0

[a] The corresponding geometries are given in Figure 3

TABLE 3: Calculated Bond Energies and Rotation Barriers

	compound						
	4 //	**4** ⊥	**4**	**5**	**6**	**8**	**9**
bond energy[a] (ZPE corrected)	63.34	90.60	64.46	59.67	65.13	65.24	113.83
rotation barrier[a] (around C_cP)				13.24	22.76	2.09	69.66

[a] All values are in kilocalorie per mole.

Thermochemical Aspects. The calculated (ZPE corrected) values of Table 3 afford supporting information for comparing the C_cP bonding in **4**−**6, 8**, and **9**. Bond energies have been calculated as the energy difference between the molecule and both fragments in their most stable electronic state (singlet or triplet).

Upon comparison of the bond energies, the most striking difference is found between the "true" double bond of **4** ⊥ (90.60 kcal mol^{-1}) and the same linkage, which drops noticeably to 64.46 kcal mol^{-1} in **4**. These values illustrate the fact that the shorter the bond, the stronger it is. But it is noteworthy that such an important variation of the bond energy is only associated with a variation of ca. 4% in bond lengths.

A much less dramatic effect is observed when dealing with **5** and **6**. A variation of ca. 2% in bond lengths now is only associated with a variation of 5.5 kcal mol^{-1}, still in favor of a stronger bond in the less conjugated compound, **6**.

The calculated rotation barriers (Table 3) of **5**, **6**, **8** and **9** provide another type of information about the actual C_cP bond. (These barriers have been estimated as the difference between the optimized planar structure and the nonoptimized structure in which the PH extremity is rotated by 90°; see Schmidt et al.[34]) In **9**, where a true double bond is present, the rotation barrier has been roughly estimated at 69.66 kcal mol^{-1}. This value drops to 13.24 kcal mol^{-1} in **5**, showing that only very little double-bond character is present. The rotation barrier in **6** is larger (22.76 kcal mol^{-1}) though remaining much smaller than that in **9**.

To conclude this part, we see that a series of converging data shows that when strong N-electron donation is present, the C_cP double-bond character vanishes. However, the comparison of **5** and **6** does provides some complexity, because a large variation of the rotation barrier magnitude (9.52 kcal mol^{-1}), associated with more or less partial C_cP double-bond character, is found for bonds whose energy difference is only 5.46 kcal mol^{-1}. We thus feel the need for a more refined description of the various effects governing the actual electronic features of the various C_cP bonds.

ELF Study of the CP Bonding

Prior to the detailed study of calculated results, a brief comment on ELF analysis of two types of usual double bonds is worthwhile. It has been shown that ELF calculations yield various types of basins, located around an attractor.[29−31] For

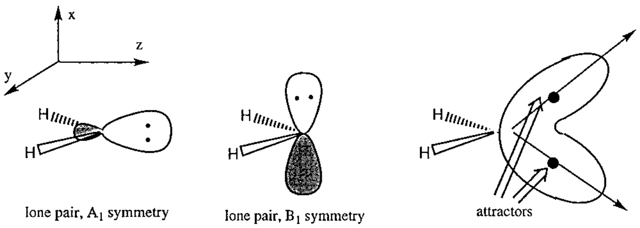

Figure 4. Schematic display of the lone-pair attractors in H_2O.

the rest of our discussion, it is important to be precise about the chemical meaning of the terminology that is used. First of all, the nature and population of the core basins, located around the heavy atoms, which are typical of the K shell for C and N atoms and K and L shells for P, will not be treated here, for the sake of conciseness. To a good approximation, they may be considered as remaining independent of the actual substitution and bonding pattern. A given valence basin will be labeled one of the following: (i) $V(X)$ when it only shares a boundary with a core basin (monosynaptic) and thus contains electrons that are not involved in a bonding process. This corresponds to the usual Lewis language for nonbonding electrons. In this case, the ideal count of electron population is 2 for a "lone pair" or 1 for an "odd electron", depending on the actual case. (ii) $V(X, Y)$ when it shares a boundary with the cores of two atoms X and Y (disynaptic). Such a basin is typical of a bond between X and Y. We will see in coming sections that its population may significantly vary, according to the actual nature of the bond. Though the classical MO language distinguishes σ and π contributions to bonding, the ELF analysis, which is based on the *total* electronic density characterizes basins and attractors without separating these types of contributions. For example, when dealing with the lone pairs of H_2O in its equilibrium C_{2v} geometry, the associated MOs are of A_1 and B_2 symmetry with the reference axes of Figure 4 (left). The molecular density obviously reflects these major localizations, but the actual resulting shape of the lone pairs is schematically displayed on the right part. Two attractors are found along oblique directions (arrows), and the beanlike three-dimensional (3D) shape of the adjacent basins corresponds to the valence-shell electron-pair repulsion solution for four pairs of electrons, two for each CH bond and two for each lone pair.[29]

When dealing with alkenes, two $V(C, C)$ basins are observed at the usual standard bond length, separately lying above and below the double-bond local plane. Whereas the electron population for a single bond is ≈1.85−1.90 e, the sum of the basins population is 3.62 e in model C_2H_4. The number of basins critically depends on the actual bond length and the repulsive interactions with neighboring linkages. For example in benzene, where the CC bond length is longer than that in C_2H_4 (1.4 vs 1.34 Å for mean values), one gets for each CC bond a single basin, centered in the middle of CC, with a population of 2.83 e, thus illustrating the Kékulé structure of this molecule.[30] These findings will be helpful for interpreting our calculated results.

ELF Study of 7−9. Let us now consider the calculated basins populations given in Table 4 for **7**−**9**. In phosphinidene itself, **7**, a population of 4.14 e is found in $V(P)$, concentrated into a single basin. This clearly shows that two lone pairs are present, yielding a resulting toric shape having the symmetry of the molecule.[31] A population of 1.85 e is found for the PH bond, showing that some density has been transferred from PH to the P lone pairs. (The sum of all contributions is not exactly 6, due to cutoffs in the integration technique). In **8**, $V(P)$ drops to 2.18 e, which lies in the typical value of a single aliphatic P lone pair. $V(C_c, P)$, which is equal to 1.76 e, is close to the usual values found in single bonds. By contrast, **9** exhibits two important changes: (i) the $V(C_c, P)$ population of 3.00 e is intermediate between that of a single CC bond (≈1.85 e) and that of a double CC bond (3.65 e) (vide supra.). The $V(P)$ population of 2.70 e is larger than that in **8**. Both data show that *partial* double-bond character is present. The latter character arises from donation of the P lone pair electrons to C_c, according to a classical back-donation scheme.

TABLE 4: Populations of the Various Valence Basins (in electrons)

	compound						
type of basin	**1**	**5**	**2**	**6**	**7**	**8**	**9**
$V(C_c)$	2.46		2.31				
$V(P)$		3.76[a]		3.62[a]	4.14	2.18	2.70
$V(N)$	0.98[a]	1.60[a]	1.27	1.82			
$V(C_c, P)$		2.60		2.53	1.76		3.00[a]
$V(C_c, N)$	2.49	2.11	2.73	2.34			
$V(N, C)$	1.93	1.87	1.56	1.56			
$V(C, C)$	3.58[a]	3.58[a]	1.87	1.87			
$V(P, H)$		1.88		1.90	1.85		
$\Sigma(C_c)$[b]	7.44	6.82	7.77	7.21			
$\Sigma(N)$	7.53	7.60	7.53	7.64			
$\Sigma(C)$	7.74	7.69	7.58	7.57		7.75[c]	7.21[c]
$\Sigma(P)$		8.24		8.06	5.99	7.88[c]	7.69[c]

[a] Sum of two basins of equal population. [b] Sum of the valence populations involving this atom. [c] All data are not reported here for the sake of shortness.

Comparison of the ELF Electronic Distributions in 1 and 2. Contour line diagrams of the ELF electronic distribution are displayed in Figure 5 (top) for **1** and **2**. First of all, it is noteworthy that in both structures a nucleophilic lone pair is located on C_c, with maximum extension in the ring plane. The corresponding basins are populated by 2.46 and 2.31 electrons in **1** and **2** (Table 4), respectively, thus showing that **1** is potentially a better σ-donor than **2**. In both molecules **1** and **2**, the $V(N)$ populations are less than 2.00 e, which shows that noticeable parts of the N lone pair densities have been transferred to C_c, thus increasing its overall local electronic density. This transfer is less effective in **2** ($V(N) = 1.27$ e) than it is in **1** ($V(N) = 0.98$ e). The large value of $V(N, C)$ in **1** (1.93) shows that the aromatic delocalization is effective, because this value is only 1.56 e in **2** where the delocalization is absent. Another measure of the aromatic delocalization is provided by the examination of $V(C_c, N)$, which is larger in **2** (2.73 e, delocalization on 3 centers) than it is in **1** (2.49 e, delocalization on 5 centers). However, both $V(C_c, N)$ values indicate the presence of a partial double bond between C_c and N, the latter being more pronounced in **2**. In **1**, a true CC double bond is present, with a population of 3.58 e, as in C_2H_4 (vide supra). The latter point seems to indicate that the CC linkage does not participate extensively to the aromatic character and mostly acts as a transmitter of the electronic effects.

Comparison of the ELF Electronic Distributions in 5 and 6. With the same conventions as those in the preceding paragraph, contour line diagrams of the ELF electronic distribution are displayed in Figure 5 (bottom) for **5** and **6**. Although ELF results do not formally separate σ and π-type effects, a qualitative comparison of the CP bonding in **5** and **6** can be made from the data of Table 4. The CP bonding is governed by two main effects: (i) a dominant strong σ-donation from C_c to the PH unit, in agreement with the nucleophilic character of both **1** and **2**, as previously pointed out, and (ii) a minor back-bonding transfer from the P lone pairs to the π system of the ring. Let us first examine the **1** and **5** couple. In **5**, the total population, $V(P) + V(P, H)$ is 5.64 e, which, with respect to the initial 6 e of isolated PH, (**7**), shows that the P atom has

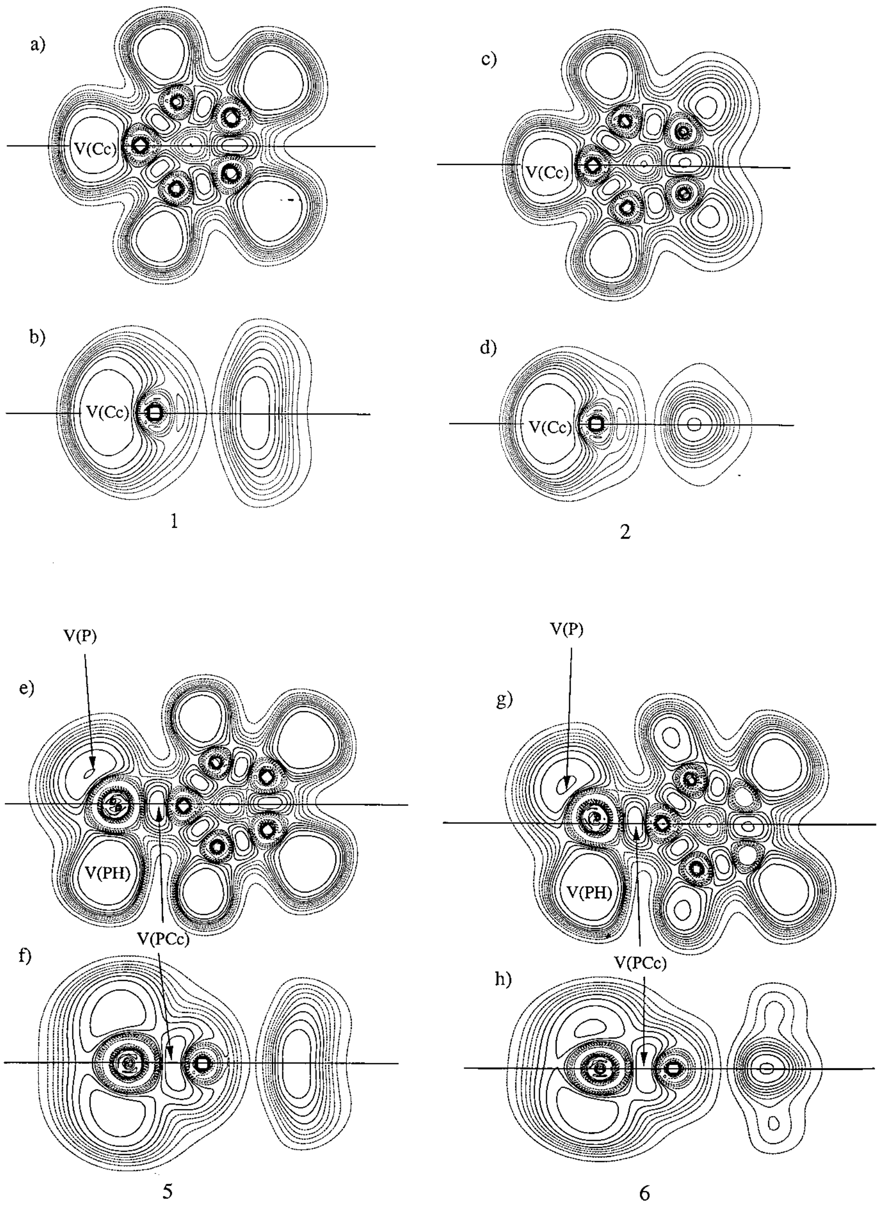

Figure 5. Contour line diagrams of the ELF electronic distributions: (a) **1** in the N$-$C$_c$$-$N plane, (b) **1** perpendicular to the N$-$C$_c$$-$N plane, (c) **2** in the N$-$C$_c$$-$N plane, (d) **2** perpendicular to the N$-$C$_c$$-$N plane, (e) **5** in the N$-$C$_c$$-$N plane, (f) **5** perpendicular to the N$-$C$_c$$-$N plane, (g) **6** in the N$-$C$_c$$-$N plane, and (h) **6** perpendicular to the N$-$C$_c$$-$N plane. Dashed contours indicate an ELF value inferior to 0.5; solid contours indicate ELF values superior to 0.5. Solid lines show the cut plan for the other diagram of the same molecule.

“lost” 0.36 e during the formation of the C$_c$$-$P bond. If one assumes the limited model in which a dative bond from C$_c$ to P, accompanied by P back-donation, is formed between the last two atoms, the overall $V(C_c, P)$ population is expected to be 2.82 e [2.46 ($V(C_c)$ in **1**) + 0.36 (afforded by P)]. Because the actually calculated $V(C_c, P)$ population is only 2.60 e, it reveals that, on a total of 0.36 e, the P atom has only given 0.14 e [2.60 − 2.46e] to form a partial double bond between C$_c$ and P, and the rest, 0.22 e, is given to the ring, thus contributing to an increased electron localization on both N atoms, or in other words a decrease of aromaticity. The same type of analysis carried out on the **2**/**6** couple shows that the total $V(P) + V(P, H)$ sum in **6** is 5.52 e. Thus, the P atom has given 0.48 e to the system with respect to isolated PH. Because the actually calculated $V(C_c, P)$ population is 2.53 e, a total of 0.22 e [2.53 − 2.31] has been provided by P to form a partial C$_c$P double bond. The remaining 0.26 e has been given to the ring, again contributing to an increased electronic localization on the N atoms. This qualitative analysis roughly shows that the C$_c$P double-bond character is twice that of **5** in **6**. These results are in very good agreement with the calculated bond lengths (1.763 Å in **5**; 1.745 Å in **6**), the bond energies (59.60 in **5**; 65.13 in **6**), and the rotation barriers (13.24 kcal mol^{-1} in **5**, 22.76 kcal mol^{-1} in **6**) (see Table 3). An apparent paradox nevertheless arises, because, despite these convergent results, the $V(C_c, P)$ basin population is smaller in **6** (2.53 e) than in **5** (2.60 e). The reason is that **2** is a less efficient σ-donor than **1** (vide supra) and thus provides less electronic density to the bulk bonding basin.

Comparative Study of NICS Values in 1 and 5

The comparison of NICS data in a series of related compounds yields a reliable measure of their aromatic character. In Table 5 typical values for various five- and six-membered rings systems are given. First of all, it is noteworthy that the results depend on both basis set and quantum mechanical technique as observed in previous studies. Accordingly, at the center of the

TABLE 5: Calculated NICS Values for 1, 5 and Various Typical Compounds

(6-31+G*) (center of the ring)		(6-31+G*) (0.5 Å above the center)	
compd	**NICS** (ppm)	compd	**NICS** (ppm)
benzene	−9,7[a]	benzene	−11.5[c]
thiophene	−13.6[a]	pyridine	−10.6[c]
furan	−12.3[a]	phosphinine	−10.2
phosphole	−5.3[a]		
pyrrole	−15.1[a]		
1	−12.7[b]	**1**	−12.5[b]
5	−10.2[b]	**5**	−8.7[b]
	(RHF/TZ)[d]		
1	−13.7[d]		
$SiC_2H_4N_2$	−10.2[d]		
$GeC_2H_4N_2$	−10.8[d]		
$ClCu-C_3H_4N_2$	−14.2[d]		
$ClCu-SiC_2H_4N_2$	−10.4[d]		
$ClCu-GeC_2H_4N_2$	−11.3[d]		

[a] Schleyer et al.[32a] [b] This work. [c] Frison et al.[36] [d] Data obtained with a different basis set and technique; see Boehme and Frenking.[35]

ring, the NICS value is −12.7 ppm for **1** in our study, whereas Boehme et al. have found −13.7 ppm with a TZ basis set.[35] Focusing our attention on the first two sets of data of Table 5, one sees that upon complexation by PH the NICS value of **1** drops to −10.2 and −8.7 ppm, when the reference point is, respectively, taken at the center of the ring or 0.5 Å above. A strikingly different trend has been observed upon complexation of **1**, $SiC_2H_4N_2$, and $GeC_2H_4N_2$ by CuCl, because the NICS values in the complex either increase (in the case of **1** and $GeC_2H_4N_2$) or remain quite constant when dealing with $ClCu-SiC_2H_4N_2$ (see Table 5, last set of entries). Our results thus show that the formation of a C_c-PH dative bond in **5**, associated with weak π-donation from PH to the ring, perturbs the overall ring aromatic character by forcing the N lone pairs to remain more localized than those in the free species **1**.

Conclusion

By use of very simple bonding models, ELF calculations provide an efficient interpretative tool for the comparison of free and complexed carbene species. Although the C_c-P bonding mode essentially results from donation of the in-plane C_c lone pair to the PH moiety, a substantial back-donation, arising from the P valence space is found. The latter effect induces a noticeable relocalization of the cycle π-electrons on both N atoms. The size of this effect in **6** is roughly twice that of **5**. With respect to **1**, the decrease of aromaticity in **5**, associated with complexation, is nicely corroborated by NICS calculations. In the same perspective, the study of ring and P-substituted systems is in progress.

References and Notes

(1) Review by: Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162.

(2) (a) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. (b) Arduengo, A. J., III; Kline, M.; Calabrese, J. C.; Davidson, F. *J. Am. Chem. Soc.* **1991**, *113*, 9704. (c) Dixon, D. A.; Arduengo, A. J., III. *J. Phys. Chem.* **1991**, *95*, 4180. (d) Arduengo, A. J., III; Rasika Dias, H. V.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530. (e) Arduengo, A. J., III; Rasika Dias, H. V.; Dixon, D. A.; Harlow, R. L.; Klooster, W. T.; Koetzle, T. F. *J. Am. Chem. Soc.* **1994**, *116*, 6812. (f) Arduengo, A. J., III; Gamper, S. F.; Tamm, M.; Calabrese, J. C.; Davidson, F.; Craig, H. A. *J. Am. Chem. Soc.* **1995**, *117*, 572. (g) Arduengo, A. J., III; Goerlich, J. R.; Marshall, W. J. *J. Am. Chem. Soc.* **1995**, *117*, 11027.

(3) Dixon, D. A.; Dobbs, K. D.; Arduengo, A. J., III; Bertrand, G. *J. Am. Chem. Soc.* **1991**, *113*, 8782.

(4) Alder, R. W.; Allen, P. R.; Murray, M.; Orpen, A. G. *Angew. Chem.* **1996**, *108*, 1211; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1121.

(5) Sauers, R. R. *Tetrahedron Lett.* **1996**, *37*, 149.

(6) Cioslowski, J. *Int. J. Quantum Chem.* **1993**, *27*, 309.

(7) Heinemann, C.; Müller, T.; Apeloig, Y.; Schwartz, H. *J. Am. Chem. Soc.* **1996**, *118*, 2023.

(8) Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, *118*, 2039.

(9) Meriem, A.; Majoral, J. P.; Revel, M.; Navech, J. *Tetrahedron Lett.* **1983**, *24*, 1975.

(10) Chermega, A. N.; Antipin, M. Y.; Struchkov, Y. T.; Boldeskul, J. E.; Sarina, T. V.; Romanenko, V. D. *Dokl. Acad. Nauk SSSR* **1984**, *278*, 1146.

(11) Povolotskii, M. I.; Tasarevich, A. S.; Bolokskul, I. E. *J. Gen. Chem. USSR* **1989**, *59*, 709.

(12) Ishmaeva, E. A.; Patsanovsky, I. I.; Romanenko, V. D.; Markovsky, L. N. *Phosphorus, Sulfur Silicon Relat. Elem.* **1990**, *49/50*, 289.

(13) Povolotskii, M. I.; Negrebetskii, V. V.; Romanenko, V. D.; Ivanchenko, V. I.; Sarina, T. V.; Markovskii, L. N. *J. Gen. Chem. USSR* **1990**, *60*, 2000.

(14) Vovna, V. I.; Alekseiko, L. N.; Gulenko, A. N.; Petrachenko, N. E.; Romanenko, V. D.; Sarina, T. V. *Russ. J. Phys. Chem.* **1992**, *66*, 1727.

(15) Romanenko, V. D.; Sanchez, M.; Ruban, A. V.; Gudima, A. O.; Povolotskii, M. I.; Mazieres, M. R.; Wolf, R. *Phosphorus, Sulfur Silicon Relat. Elem* **1993**, *76*, 29.

(16) Povolotskii, M. A.; Rozhenko, A. V.; Polovinko, V. V.; Chemeya, A. N. *Phosphorus, Sulfur Silicon Relat. Elem.* **1996**, *109−110*, 617.

(17) Arduengo, A. J., III; Krafczyk, R.; Marshall, W. J.; Schmutzler, R. *J. Am. Chem. Soc.* **1997**, *119*, 3381.

(18) Arduengo, A. J., III; Rasika Dias, H. V.; Calabrese, J. C. *Chem. Lett.* **1997**, 143.

(19) Arduengo, A. J., III; Calabrese, J. C.; Cowley, A. H.; Rasika Dias, H. V.; Goerlich, J. R.; Marshall, W. J.; Bernhard Riegel, B. *Inorg. Chem.* **1997**, *36*, 2151.

(20) Arduengo, A. J., III; Carmalt, C. J.; Clyburne, J. A. C.; Cowley, A. H.; Pyati, R. *Chem. Commun.* **1997**, 981.

(21) Decken, A.; Carmalt, C. J.; Clyburne, J. A. C.; Cowley, A. H. *Inorg. Chem.* **1997**, *36*, 3741.

(22) Frison, G.; Mathey, F.; Sevin, A. *J. Organomet. Chem.* **1998**, *570*, 225 and references therein.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, rev. c.3; Gaussian, Inc.: Pittsburgh, PA, 1995.

(24) Stevens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(25) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta (Berlin)* **1973**, *28*, 213.

(26) (a) Bauschlicher, C. W., Jr.; Partridge, H. *J. Chem. Phys.* **1995**, *103*, 1788. (b) Wong, M. W. *Chem. Phys. Lett.* **1996**, 256, 391.

(27) (a) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (b) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736. (c) Reed, A. E.; Curtis, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(28) TopMod is a series of programs written in our group by: Noury, S.; Krokidis, X.; Fuster, F.; Silvi, B. 1997. Available upon request at sevin@lct.jussieu.fr.

(29) (a) Silvi, B.; Savin, A. *Nature* **1994**, *371*, 683. (b) Savin, A.; Jespen, J.; Andersen, O. K.; Preuss, H.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 187. (c) Savin, A.; Nesper, R.; Wengert, S.; Fässler, T. F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1809.

(30) Savin, A.; Silvi, B.; Colonna, F. *Can. J. Chem.* **1996**, *74*, 1088.

(31) The same type of volume is found in molecules having a C_∞ symmetry rotation axis such as Cl_2, for example. Krokidis, X.; Silvi, B.; Dezarnaud−Dandine, C.; Sevin, A. *New J. Chem.* **1998**, 1341.

(32) (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996,** 118, 6317. (b) Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. R. v. E.; Malkin, V. G.; Malkina, O. *J. Am. Chem. Soc.* **1997**, 119, 12669.

(33) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; J. Wiley and Sons: New York, 1986.

(34) Schmidt, M. W.; Truong, P. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5217.

(35) Boehme, C.; Frenking, G. *Organometallics* **1998**, *17*, 5801.

(36) Frison, G.; Sevin, A.; Avarvari, N.; Mathey, F.; Le Floch, P. *J. Org. Chem.* **1999**, 64, 5524.