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Substituent effects in polarized phosphaalkenes: a theoretical study of aminocarbene–phosphinidene adducts

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This paper is kindly dedicated to Professor François Mathey, for his seminal influence, and fruitful long-lasting partnership

Abstract

The effect of substituent has been theoretically explored in the case of polarized phosphaalkenes formed with an aminocarbene and a phosphinidene. The shape of the experimentally characterized structures has been explained in terms of electronic and steric effects. The balance between σ-donation and π-back-donation as a function of the substituent has been explored by the use of electron localization function (ELF) analysis and correlated with the bond dissociation energy and geometrical structure. The aromaticity of the carbene ring, obtained by NICS calculation, has been achieved. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Density functional theory (DFT) calculation; Polarized phosphaalkene; Aminocarbene complexes; Aromaticity; Bonding analysis; Electron localization function (ELF)

1. Introduction

Since the synthesis and characterization of the first imidazol-2-ylidene by Arduengo and co-workers [1], their coordination to almost all elements of the periodic table has been achieved [2,3]. In transition metal complexes, these carbenes play the role of a phosphine ligand due to the presence of a nucleophilic lone pair on the carbenic carbon. When dealing with interaction with main group elements [3,4], the bonding is more peculiar and is still the subject of intensive controversy [5]. When the main group fragment is formed by a structure isolobal to that of a carbene, a formal double bond is formed, which possesses particular structure and reactivity [6–9]. In most cases, the length of this 'double bond' is not significantly shorter than the corresponding single bond and the bond is polarized according to the limiting resonance structures displayed in Fig. 1.

During our study of the coordination of phosphinidene fragments PR on organometallic complexes [10], we became interested in the possibility of coordination of phosphinidenes to a diaminocarbene [7–9]. Recently, we have examined the complexation of the parent phosphinidene PH to various diaminocarbenes (imidazol-2-ylidene, imidazolin-2-ylidene, $(NH_2)_2C$) [11]. We have shown that the C–P bonding mode results from donation of the in-plane carbene lone pair to the PH moiety and from a substantial back-donation from the P valence space to the cycle. The use of topological analysis of the electron localization function (ELF) [12] permits quantitative evaluation of both effects. In the case of the imidazol-2-ylidene, we have also shown that the back-donation, which competes with the delocalization of the nitrogen lone pairs in the ring, is impeded by the carbene aromaticity.

However, during this preliminary study, we did not examine the effects of substitution on nitrogen and on phosphorus atoms. Consequently, our optimized model structures, characterized by an absence of twist of the substituent R on P, a P–C bond length that is too short, and a C–P–R bond angle that is too open, show differences with the crystallographic data given in Fig. 2 [7,9]. In experimental structures, the role of substituents is important. The carbon–phosphorus bond is noticeably influenced by substitution on the cycle (1–6 = 1.794 Å for **1-PPh** and 1.763 Å for **2-PPh**) and

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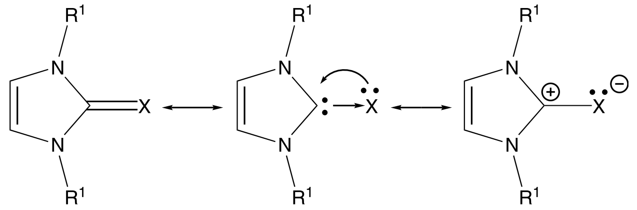
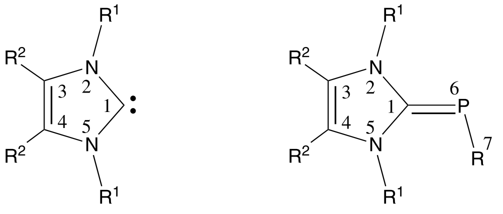


X = CR$_2$, SiR$_2$, GeR$_2$, SnR$_2$, PbR$_2$, PR, AsR, O, S, Se, Te

Fig. 1. Limiting resonance structures involved in a double bond between imidazol-2-ylidene and main group element.



1 R^1 = R^2 = Me
2 R^1 = Mes, R^2 = H

1-PPh R = Ph R^1 = R^2 = Me
2-PPh R = Ph R^1 = Mes, R^2 = H
2-PCF$_3$ R = CF$_3$ R^1 = Mes, R^2 = H

Fig. 2. Structural features of imidazol-2-ylidene and corresponding complexes with phosphinidene whose crystallography data are described in the literature [7,9]. See Table 1 for detailed geometry.

on the phosphorus atom (1–6 = 1.763 Å for **2-PPh** and 1.784 Å for **2-PCF$_3$**) (Table 1). We thus have decided to study the effects of substituents and to examine the changes they bring to the electronic distribution. Two kinds of substituents have been introduced on N and/or on P atoms in our model: methyl groups are used to account for steric effects and CF$_3$ groups introduce electronic effects as in the experimental structure (Fig. 3).

This study is aimed at answering the following questions: May experimental structures be reproduced by standard quantum mechanical calculations including substituents on N and/or P? Do substituent effects modify the electronic distribution compared to parent species?

2. Methodology

All calculations were carried out with the GAUSSIAN 94 [13] or GAUSSIAN 98 [14] suite of programs using the 6-31G* basis set [15] containing six cartesian d functions. Geometry optimizations were performed utilizing Becke's hybrid three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang and Parr (B3LYP) [16]. A vibrational analysis was performed at each stationary point found, to confirm its identity as an energy minimum (NIM = 0). The harmonic frequencies were used with a scaling factor of 0.98 to calculate the zero-point energies [17]. The aro-

Table 1
Experimental and calculated bond lengths (Å), bond and dihedral angles (°) at the B3LYP/6-31G* level for carbenes **1**–**5** and their corresponding complexes with phosphinidenes PR (R = H, CH$_3$, CF$_3$ or Ph)

	1–6	1–2	1–5	6–7	1–2–5	1–6–7	5–1–6–7
1 [a]		1.363	1.363		101.5		
1-PPh [b]	1.794	1.365	1.361	1.817	104.7	102.3	46
2 [a]		1.365	1.371		101.4		
2-PPh [c]	1.763	1.369	1.378	1.839	104.0	99.9	26.2
2-PCF$_3$ [c]	1.784	1.370	1.365	1.845	104.5	101.7	28.2
3 [d]		1.372	1.372		99.9		
3-PH [d]	1.763	1.378	1.377	1.432	103.0	92.5	0.0
3-PCH$_3$	1.758	1.381	1.379	1.890	103.1	97.4	0.0
3-PCF$_3$	1.778	1.371	1.368	1.879	103.7	95.6	10.8
4		1.372	1.373		100.7		
4^E-PH	1.766	1.378	1.376	1.432	103.9	92.3	0.0
4^E-PCH$_3$	1.761	1.381	1.378	1.890	104.0	97.3	0.0
4^E-PCF$_3$	1.780	1.372	1.369	1.880	104.6	95.5	4.4
4^Z-PH	1.767	1.379	1.380	1.426	103.8	94.3	0.1
4^Z-PCH$_3$	1.769	1.381	1.384	1.892	103.6	103.4	27.0
4^Z-PCF$_3$	1.789	1.373	1.373	1.882	104.0	101.0	34.2
5		1.373	1.373		101.5		
5-PH	1.770	1.379	1.380	1.426	104.7	94.0	0.0
5-PCH$_3$	1.773	1.385	1.386	1.891	104.3	103.8	22.2
5-PCF$_3$	1.792	1.379	1.376	1.882	104.7	102.1	28.8

For numbering of the atoms, see Figs. 2 and 3.
[a] Ref. [20].
[b] Ref. [9].
[c] Ref. [7].
[d] Ref. [11].

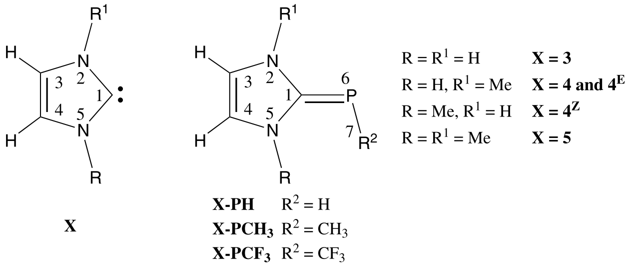


Fig. 3. Molecules studied in this work.

matic character was evaluated by computing the nucleus-independent chemical shift (NICS, GIAO-SCF/6-31+G*//B3LYP/6-31G*) at the center of the five-membered ring [18].

ELF calculations were achieved using the wfn output of B3LYP runs, using the TOPMOD series of programs [19]. In the ELF method, the molecular space is divided into various types of basins located around an attractor. Core basins, labeled C(X) and located around the heavy atoms, which are typical of the K shell for C, N and F 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 and thus contains electrons that are not involved in a bonding process. This corresponds to the usual Lewis language for nonbonding electrons. In that case, the ideal count of electron is 2 for a “lone pair” or 1 for an “odd electron”, depending on the actual case. (ii) V(X, Y) when the basin shares a boundary with the cores of two atoms X and Y. Such a basin is typical of a bond between X and Y. We will see in coming sections that its population may vary significantly, 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 contribution. For example, 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 plan. A more detailed presentation of the method and the interpretation of the results are given in the literature [12].

3. Results and discussion

Our results are given according to the following order. We first discuss the geometry of molecules bearing CH_3 and CF_3 substituents and compare them with the experimental ones. Then, we discuss the influence of substituents on the electronic structure of these molecules based on bond dissociation energy, ELF and aromaticity analysis.

3.1. Geometry

Fig. 4 shows the optimized geometry of carbenes **3**–**5** and their corresponding complexes with phosphinidenes PR (R = H, CH_3 and CF_3). The calculated bond lengths and angles are given in Table 1, as well as those of experimental structures of **1**, **2**, **1-PPh**, **2-PPh** and **2-PCF$_3$**. For complexes **4-PR**, we calculated Z and E structures around the C1–P6 bond, noted respectively, **4^Z-PR** and **4^E-PR**, so as to distinguish between electronic and steric influence of substituents. All structures displayed in Fig. 4 are true minima (NIM = 0) on their respective potential energy surfaces.

The calculations show that a substituent placed at the N2 position has very little influence on the geometry of molecules, as illustrated by the quasi-identity of structures **3-PR** and **4^E-PR**, and of structures **4^Z-PR** and **5-PR**. This also shows that a methyl substituent placed on the carbene ring has no noticeable electronic influence. This is confirmed by the only very small differences found between carbenes **3**, **4** and **5**, as well as by the structural similarity of **3-PH** with **4^Z-PH** and **5-PH**, where the methyl substituent is located on N5. The loss of planarity in **4^Z-PCH$_3$** and **5-PCH$_3$**, with respect to **4^E-PCH$_3$**, thus exclusively results from a steric effect. The increase of the 1–6–7 angle by about 6–7° in these compounds is another consequence of this effect.

The electronic influence of a methyl group is greater when it is located on P than on the ring. The comparison of **3-PH** and **3-PCH$_3$**, or of **4^E-PH** and **4^E-PCH$_3$**, reveals a small shortening of the C1–P6 bond as well as a slight increase of the C1–N2/5 bond lengths. This is consistent with an increase of the back-donation from PCH_3 with respect to PH. A steric effect is also present, resulting in an increase of the 1–6–7 angle in **3-PCH$_3$** and **4^E-PCH$_3$**, respectively, compared to **3-PH** and **4^E-PH**. As a consequence of the strong back-donation of PCH_3, no twist around the C1–P6 bond is observed.

The strong electron-withdrawing group CF_3 brings important changes in the geometry of the polarized phosphaalkene. The C1–P6 bond length increases by 0.02 Å and C1–N2/5 bonds are slightly longer, compared with the cases of R = H or CH_3. Those effects are opposite to those of CH_3 and indicate a lowering of the back-donation to the ring of the PCF_3 fragment and, accordingly, a lowering of the double-bond character of the C1–P6 bond.

Other structural features confirm the electronic effects. The steric repulsion between CF_3 and H groups in **3-PCF$_3$** and **4^E-PCF$_3$** leads to a less pronounced increase of the 1–6–7 angle with respect to the case of R = CH_3, because the CF_3 group is now slightly twisted around the C1–P6 bond, by about 5–10°. This greater facility of twist is also shown in **4^Z-PCF$_3$** and **5-PCF$_3$** where the dihedral angle N5–C1–P6–C7 is increased to 29–34° compared to the 22–27° in **4^Z-PCH$_3$** and **5-PCH$_3$**. Finally, the lowering of the back-donation should induce a greater aromaticity of the carbenic cycle (vide infra). This might be shown by the almost planarity of N5 in **4^Z-PCF$_3$** and **5-PCF$_3$** ($\Sigma N \geq 359.8°$) whereas the sum of the angles around N5 decreases to 358° in **4^Z-PCH$_3$** and **5-PCH$_3$**.

The comparison of our calculated structures with the experimental ones has shown that the differences observed in the case of **3-PH** no longer persist when substituents are present. Thereby the structure of **5-PCF$_3$** is very close to that of **2-PCF$_3$**, and displays the same structural characteristics as the experimental molecule (twist of the substituent R on P, short P–C bond length, and acute C–P–R bond angle). These results confirm the accuracy of our model and allow for further discussion.

3.2. Electronic structure

The second column of Table 2 gives the dissociation energies ($D°$) of the C1–P6 bond formed. As noted previously for the parent compound **3-PH** [11], the energy of the CP bond formed between an aminocarbene and a phosphinidene (49–68 kcal mol^{-1}) is approximately half that of the bond between an alkylcarbene and a phosphinidene (113–117 kcal mol^{-1}). A closer examination of the computed values reveals interesting trends. (i) Substitution of a hydrogen atom by a methyl group on N only very slightly in-

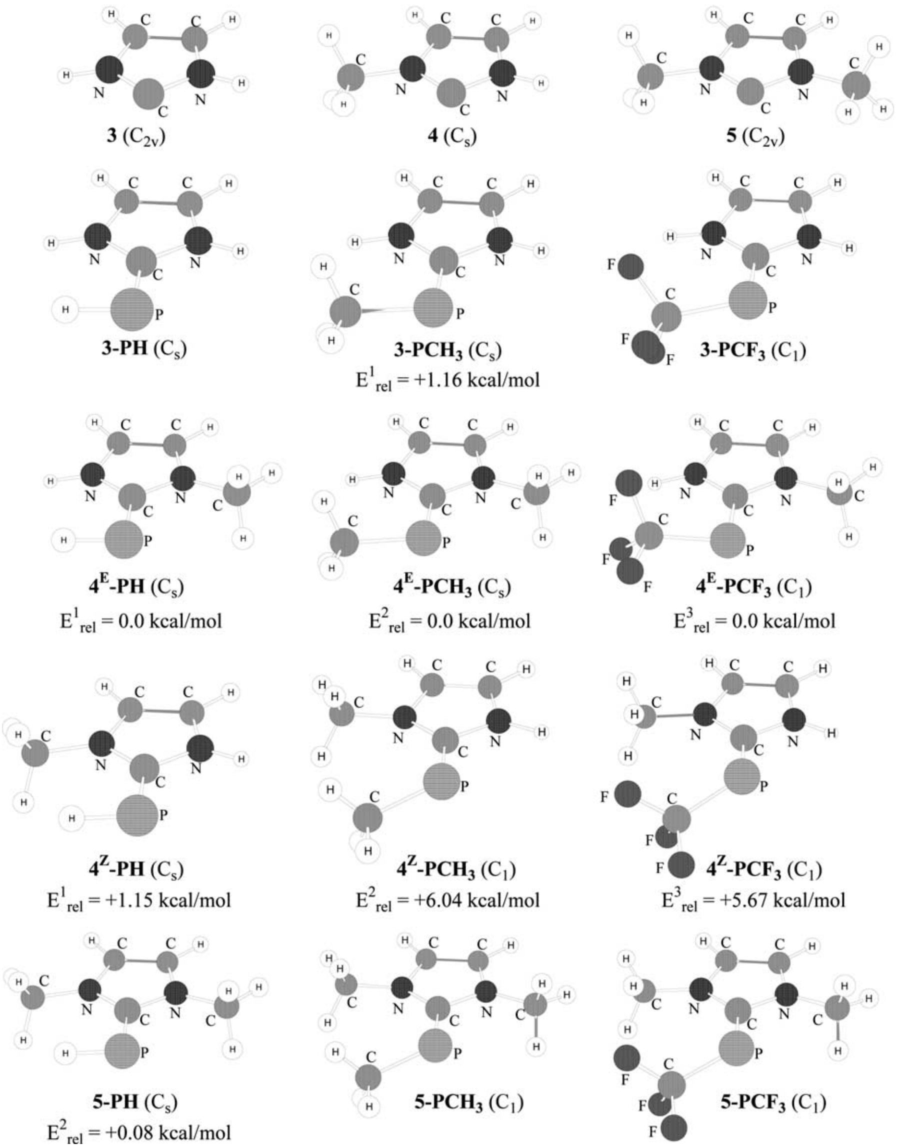


Fig. 4. Optimized equilibrium structures (B3LYP/6-31G*) of carbenes **3**–**5** and their corresponding complexes with phosphinidenes PH, PCH$_3$ and PCF$_3$. The geometrical parameters are shown in Table 1.

Table 2
Bond dissociation energy, population of ELF basins and aromaticity calculated at the B3LYP/6-31G* geometry for carbenes **3**–**5**, their corresponding complexes with phosphinidenes PR (R = H, CH_3, CF_3), and some classical phosphaalkenes

	$D°$(C1–P6) [a]	V(C1, P6) [b]	V(P6) [b]	Donation [c]	Back-donation [d]	NICS [e]
CH_2PH [f]	113.83	2.97 [g]	2.70	1.67	−1.30	
CH_2PCH_3	113.15	3.12 [g]	2.72	1.77	−1.35	
CH_2PCF_3	116.98	3.03 [g]	2.81	1.79	−1.24	
3 [f]		2.46 [h]				−12.7
3-PH [f]	59.67	2.60	3.76 [g]	2.24	−0.36	−10.2
3-PCH_3	54.41	2.71	3.72 [g]	2.29	−0.42	−9.9
3-PCF_3	66.80	2.70	3.72 [g]	2.36	−0.34	−11.2
4		2.48 [h]				−12.2
4^{E}-PH	60.61	2.61	3.74 [g]	2.26	−0.35	−10.8
4^{E}-PCH_3	55.36	2.83	3.64 [g]	2.34	−0.49	−10.5
4^{E}-PCF_3	67.84	2.73	3.71 [g]	2.40	−0.33	−11.7
4^{Z}-PH	59.46	2.56	3.74 [g]	2.21	−0.35	−10.7
4^{Z}-PCH_3	49.32	2.72	3.74 [g]	2.30	−0.42	−10.5
4^{Z}-PCF_3	62.17	2.66	3.79 [g]	2.40	−0.26	−11.8
5		2.45 [h]				−11.7
5-PH	60.33	2.62	3.70 [g]	2.26	−0.36	−11.4
5-PCH_3	49.83	2.81	3.68 [g]	2.35	−0.46	−11.0
5-PCF_3	62.48	2.72	3.78 [g]	2.47	−0.25	−12.3

For numbering of the atoms, see Figs. 2 and 3.

[a] Bond dissociation energy (kcal mol^{-1}) based on most stable state of fragments (singlet for aminocarbenes, triplet for CH_2 and free phosphinidenes [21]) and ZPE corrected.

[b] Population of basins in electrons.

[c] Donation of the carbene fragment into the C1–P6 bond, calculated as the difference of population of V(C1, P6) and the value of back-donation.

[d] Back-donation of the phosphinidene fragment into the C1–P6 bond, calculated as the difference of population of the phosphinidene before and after complexation on the carbene.

[e] Computed at the GIAO-SCF/6-31+G*//B3LYP/6-31G* at the center of the carbene ring.

[f] Ref. [11].

[g] Sum of two equivalent basins.

[h] Population of V(C1).

creases $D°$ (by less than 1 kcal mol^{-1}) as long as no structural distortion (large variation of the dihedral angle 5–1–6–7) is observed. (ii) The steric repulsion between CH_3 and either the second CH_3 or CF_3 may be evaluated around 6 kcal mol^{-1}, which corresponds to the decrease of $D°$ due to the opening of the dihedral angle 5–1–6–7. (iii) The dissociation energy $D°$ is greatly influenced by the substitution on P in the order $D°(R = CF_3) > D°(R = H) > D°(R = CH_3)$.

3.3. ELF analysis

This last result is surprising if one refers to the C1–P6 bond length: depending on the substituent R on P, the longer the C1–P6 bond, the higher its dissociation energy. In order to analyze in detail the origin of this peculiarity, we have quantitatively examined the σ-donation and the π-back-donation as a function of the substituent through a topological analysis of the ELF function. In this aim we have evaluated the π-back-donation of the phosphinidene fragment as resulting from the difference of population of its basins before and after complexation with the carbene. On the same ground, the σ-donation of the carbene had been evaluated as the difference of the population of C1–P6 bond and the value of π-back-bonding contribution (Table 2).

First of all, as for σ-donation, we see that the population of the lone pair of the free carbene is not significantly influenced by the substitution on nitrogen. Secondly, for each kind of carbene, we may notice that the population of V(C1, P6) is not correlated with the π-back-bonding ability of the various phosphinidenes. This shows that the σ-donation of the carbene is influenced by the substituent on P. The calculation of the actual σ-donation confirms these tendencies. For each kind of carbene, the σ-donation, relative to H (2.21–2.26 electrons), varies up to 0.21 electron, whereas this variation is limited to 0.11 electron for each kind of R (H, CH_3 and CF_3). The σ-donation is higher for R = CF_3 (2.36–2.47 e) than for CH_3 (2.29–2.35 e). This is obviously in agreement with the (group-) electronegativity of H (2.1), CH_3 (2.55) and CF_3 (2.71) [22]. We thus see that the level of σ-donation may neither account for the C1–P6 bond length nor the value of the dissociation energy of this bond.

A better argument is found upon examining the π-back-donation and its influence on the electronic delocalization in the carbene ring. On the one hand, the variation of the total PR population confirms what might be induced from the examination of the geometry parameters. PCH_3 gives more electron (0.42–0.49 e) than PH (0.35–0.36 e) and even more than PCF_3 (0.25–0.34 e). The C1–P6 bond length is well correlated with the magnitude of this back-donation. On the other hand, as previously noted [11], the π-back-donation induces a decrease of delocalization in the aromatic carbene ring.

The measure of the NICS at the center of the ring confirms the latter effect: for each kind of carbene, the higher the π-back-donation of the PR group, the lower the aromaticity of the carbene ring. We may even notice an increase of aromaticity in the single case of **5-PCF$_3$** where the back-donation of PR (0.25 e) is lower than the difference of the population of V(C1, P6) compared to V(C1) in the free carbene (0.27 e).

The formation of the C1–P6 bond is accompanied by a modification of the aromatic stabilization of the 5-membered ring, which mostly depends on the substituent R on P. The bond dissociation energy $D°$ takes into account this loss of aromaticity which is well correlated with the level of π-back-donation. Finally, the decrease of $D°$(C1–P6) concurrently with the decrease of the bond length might be explained by the modification of aromaticity. At last, we could notice that the π-back-donation decreases in the case of a twist around the C1–P6 bond. This is the result of the decrease of the overlap between the lone pair of the phosphorus atom with the p atomic orbital on C1. This leads to an increase of the population of the lone pair of P.

4. Conclusion

To the questions examined at the beginning of this study we may propose qualitative answers. Our calculated geometries may be satisfactorily compared with the crystallographic structures, thus taking into account the influence of substituents. The model substituents introduced in this study give a good account for the general experimental trends.

CH_3 group has negligible electronic influence when introduced on the nitrogen, but plays a noticeable role in the twist of the C1–P6 bond due to steric repulsion. Compared to the parent system, substituted systems possess the same kind of donor–acceptor CP bond. However, the extent of electronic donation and back-donation is influenced by the substituent, especially those bonded by the phosphorus atom. On the one hand, an increase of the substituent electronegativity of R on P induces an increase of the σ-donation of the carbene. On the other hand, the level of the π-back-donation of the phosphinidene is correlated with the π-donating ability of R, as well as, indirectly, by the steric interaction. The bond length of the PC bond is mainly governed by the π-back-donation, as well as the dissociation energy of the bond, which includes the loss of delocalization in the ring of the carbene.

References

[1] (a) A.J. Arduengo III, Acc. Chem. Res. 32 (1999) 913;
(b) A.J. Arduengo III, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361.

[2] (a) W.A. Herrmann, C. Köcher, Angew. Chem. Int. Ed. Engl. 36 (1997) 2163;
(b) D. Bourissou, O. Guerret, F.P. Gabbaï, G. Bertrand, Chem. Rev. 100 (2000) 39.

[3] C.J. Carmalt, A.H. Cowley, Adv. Inorg. Chem. 50 (2000) 1.

[4] A.H. Cowley, Pure Appl. Chem. 70 (1998) 765.

[5] P.D. Boyle, S.M. Godfrey, J. Chem. Soc. Dalton Trans. (2000) 1959.

[6] (a) A.J. Arduengo III, F. Davidson, H.V.R. Dias, J.R. Goerlich, D. Khasnis, W.J. Marshall, T.K. Prakasha, J. Am. Chem. Soc. 119 (1997) 12742;
(b) A.J. Arduengo III, J.R. Goerlich, W.J. Marshall, Liebigs Ann./Recueil (1997) 365;
(c) W.M. Boesveld, B. Gehrhus, P.B. Hitchcock, M.F. Lappert, P.v.R. Schleyer, Chem. Commun. (1999) 755;
(d) N. Kuhn, H. Bohnen, J. Kreutzberg, D. Bläser, R. Boese, J. Chem. Soc. Chem. Commun. (1993) 1136;
(e) A.J. Arduengo III, H.V.R. Dias, J.C. Calabrese, F. Davidson, Inorg. Chem. 32 (1993) 1541;
(f) F. Stabenow, W. Saak, M. Weidenbruch, Chem. Commun. (1999) 1131;
(g) N. Kuhn, T. Kratz, R. Bläser, R. Boese, Chem. Ber. 128 (1995) 245;
(h) A. Schäfer, M. Weidenbruch, W. Saak, S. Pohl, J. Chem. Soc. Chem. Commun. (1995) 1157;
(i) N. Kuhn, G. Henkel, T. Kratz, Chem. Ber. 126 (1993) 2047;
(j) D.J. Williams, M.R. Fawcett-Brown, R.R. Raye, D.V. Derveer, Y.T. Pang, R.L. Jones, K.L. Bergbauer, Heteroatom Chem. 4 (1993) 409;
(k) D. Enders, K. Breuer, G. Raabe, J. Runsink, J.H. Teles, J.P. Melder, K. Ebel, S. Brode, Angew. Chem. Int. Ed. Engl. 34 (1995) 1021;
(l) G.B. Ansell, D.M. Forkey, D.W. Moore, J. Chem. Soc. Chem. Commun. (1970) 56.

[7] A.J. Arduengo III, J.C. Calabrese, A.H. Cowley, H.V.R. Dias, J.R. Goerlich, W.J. Marshall, B. Riegel, Inorg. Chem. 36 (1997) 2151.

[8] A.J. Arduengo III, C.J. Carmalt, J.A.C. Clyburne, A.H. Cowley, R. Pyati, Chem. Commun. (1997) 981.

[9] A.J. Arduengo III, H.V.R. Dias, J.C. Calabrese, Chem. Lett. (1997) 143.

[10] G. Frison, F. Mathey, A. Sevin, J. Organomet. Chem. 570 (1998) 225.

[11] G. Frison, A. Sevin, J. Phys. Chem. A 103 (1999) 10998.

[12] (a) A.D. Becke, K.E. Edgecombe, J. Chem. Phys. 92 (1990) 5397;
(b) B. Silvi, A. Savin, Nature 371 (1994) 683;
(c) A. Savin, R. Nesper, S. Wengert, T.F. Fässler, Angew. Chem. Int. Ed. Engl. 36 (1997) 1809.

[13] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y.

Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, GAUSSIAN 94, Revision D.4, Gaussian, Inc., Pittsburgh, PA, 1995.

[14] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 98, Revision A.7, Gaussian, Inc. Pittsburgh, PA, 1998.

[15] P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1973) 213.

[16] (a) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785;
(b) A.D. Becke, J. Chem. Phys. 98 (1993) 5648.

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

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

[19] S. Noury, X. Krokidis, F. Fuster, B. Silvi, TOPMOD package, Université P. et M. Curie, 1997.

[20] A.J. Arduengo III, H.V.R. Dias, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 114 (1992) 5530.

[21] The calculated singlet–triplet energy (ZPE corrected) differences of the free phosphinidenes PH, PCH_3 and PCF_3 are, respectively, 33.46, 29.44 and 29.43 kcal mol^{-1}. As suggested by one referee, these values have to be taken into account to evaluate the actual strength of the P–C bonds as the P–R fragments must bond to the *N*-heterocyclic carbene as singlet species.

[22] R.J. Boyd, S.L. Boyd, J. Am. Chem. Soc. 114 (1992) 1652.