

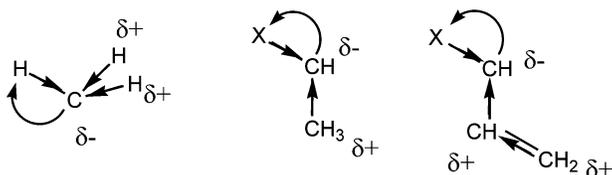
Negative Hyperconjugation in Phosphorus Stabilized Carbanions

Tom Leyssens* and Daniel Peeters

Laboratoire de Chimie Quantique, Université Catholique de Louvain,
Place Louis Pasteur 1, B-1348 Louvain-la-Neuve, Belgium

t.leyssens@chim.ucl.ac.be

Received December 10, 2007



The electronic Fukui function is used to give qualitative electronic proof on the existence of back-bonding from the carbon lone pair toward the σ^* P–Y and P–O orbitals in phosphorus stabilized carbanions. NBO analyses are used to investigate the energetic, electronic, and structural impacts of this negative hyperconjugation interaction. The observed energetic stabilization can indeed be attributed to the electronic delocalization of the lone pair toward the antibonding orbitals. This delocalization is furthermore responsible for the shorter P–C bonds, longer P–Y (P–O) bonds, and wider Y–P–Y angles observed for the anionic compounds compared to their neutral counterparts. From the electronic NBO analysis it becomes clear that phosphorus containing functional groups are best described as σ donor/ π acceptors.

Introduction

Phosphorus containing functional groups of the $-PY_2$ and $-POY_2$ type have been known for many years to be highly effective at stabilizing adjacent carbanion centers.¹ This has been widely exploited in organic synthesis,^{2,3} to the extent that P-stabilized carbanions now rank among some of the most useful reagents for a wide range of important organic transformations, such as the Horner or Horner–Wadsworth–Emmons reactions, which employ lithiated phosphine oxides and lithiated (thio)phosphonates/phosphoramides, respectively, for the olefination of carbonyl compounds.^{4–6}

The ability of third row heteroatoms to stabilize an adjacent carbanion has been variously attributed to (i) electrostatic interactions,⁷ (ii) $d\pi-p\pi$ interactions,^{8,9} (iii) negative hypercon-

jugation (delocalization of the negative charge into low lying σ^* P–Y and P–O orbitals),¹⁰ and (iv) the high polarizability of these elements.¹¹ Due to the highly electropositive character of the third period atoms, the first of these ideas was long believed to explain the observed stabilization. However, as no stabilization is observed for other compounds showing a similar $P^{\delta+}-C^{\delta-}$ pattern such as lithiated carbanions^{12,13} and the highly ionic unsaturated organophosphorus compounds,^{14,15} this idea became discarded. As for the participation of the phosphorus 3d orbitals, various theoretical studies have shown that these are too high in energy for efficient overlap with the lone pair orbital at the carbanion center.^{16,11,17,18} The *d* orbitals merely serve as polarization functions, increasing the flexibility of the basis sets used in these studies. The general consensus nowadays

(1) Izod, K. *Coord. Chem. Rev.* **2002**, *227*, 153–173.
 (2) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863.
 (3) Katritzky, A. R.; Piffl, M.; Lang, H.; Anders, E. *Chem. Rev.* **1999**, *99*, 665–722.
 (4) Horner, L.; Hoffmann, H.; Wippel, H. G.; Klahre, G. *Chem. Ber.* **1958**, *91*, 61.
 (5) Horner, L.; Hoffmann, H.; Wippel, H. G.; Klahre, G. *Chem. Ber.* **1959**, *92*, 2499.
 (6) Wadsworth, W. S.; Emmons, W. D. *J. Am. Chem. Soc.* **1961**, *83*, 1783.
 (7) Denmark, S. E.; Cramer, C. J. *J. Org. Chem.* **1990**, *55*, 1806–1813.
 (8) Johnson, A. W.; Jones, H. L. *J. Am. Chem. Soc.* **1968**, *90*, 5232.
 (9) Cheng, J. P.; Liu, B.; Zhao, Y.; Sun, Y.; Zhang, X. M.; Lu, Y. *J. Org. Chem.* **1999**, *64*, 604.

(10) Dobado, J. A.; Martinez-Garcia, H.; Molina, J. M.; Sundberg, R. J. *Am. Chem. Soc.* **2000**, *122*, 1144.
 (11) Streitwieser, A., Jr.; Williams, J. E., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 191–192.
 (12) Streitwieser, A., Jr.; Rajca, A.; McDowell, R. S.; Glaser, R. J. *Am. Chem. Soc.* **1987**, *109*, 4184–4188.
 (13) Wiberg, K. B.; Castejon, H. *J. Am. Chem. Soc.* **1994**, *116*, 10489–10497.
 (14) Leyssens, T.; Peeters, D. *THEOCHEM* **2004**, *673*, 79–86.
 (15) Leyssens, T.; Peeters, D. *THEOCHEM* **2004**, *686*, 71.
 (16) Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467.
 (17) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434.
 (18) Gilheany, D. G. *Chem. Rev.* **1994**, *94*, 1339–1375.

appears to be that carbanion stabilization by phosphorus containing functional groups is due to a combination of negative hyperconjugation and polarization effects.¹⁰

The existence of a π -back-bonding interaction from the carbanion lone pair to the σ^* antibonding P–Y (P–O) orbitals has been justified using indirect energetic as well as structural evidence, comparing the carbanions with their neutral counterparts. The energetic stabilization of the methyl anion by P-functional groups has been investigated through the use of the isodesmic reaction $\text{CH}_3\text{X} + \text{CH}_3^- \rightarrow \text{CH}_2\text{X}^- + \text{CH}_4$. Calculations at the QCISD(T)/6-31+G*/MP2/6-31+G* level including zero-point energy corrections show a stabilization of 21.3 kcal/mol for $\text{X} = -\text{PH}_2$.¹⁹ A comparable result²⁰ (23.1 kcal/mol) has been found at the MP2 level of theory using a similar basis set. The $-\text{P}(\text{OH})_2$, $-\text{PO}(\text{OH})_2$,²⁰ and $-\text{PO}(\text{NH}_2)_2$ ^{21,22} functional groups yield an even stronger stabilization energy of, respectively, 41.9, 46.4, and 39.9 kcal/mol. This important stabilization of carbanions by third row functional groups has been confirmed by an experimental electron photodetachment study of α -silyl carbanions,²³ showing a stabilization of 20 kcal/mol. From a structural point of view, the shorter P–C(carbanion), the longer P–Y (P–O), and the wider Y–P–Y angles of the anionic compounds compared to the neutral hydrogenated compounds,^{7,15,18,24,25,26,27,28,29} have been used to justify the presence of negative hyperconjugation. These structural variations are indeed consistent with an increased population of the σ^* P–Y and σ^* P–O orbitals.

Energetic and structural variations between neutral and anionic compounds are due to changes in the total bonding interaction, including σ , electrostatic, as well as π interactions.²⁸ Although the structural and energetic observations mentioned above are consistent with the idea of negative hyperconjugation, they cannot be seen as direct proof of such, nor is it clear to what extent this back-bonding interaction is responsible for the observed variations. The goal of the present paper is therefore not only to give straightforward evidence concerning the existence of π back-bonding in phosphorus stabilized carbanions but also to investigate to what extent this interaction explains the observed structural and energetic variations.

As negative hyperconjugation is nothing more than a form of electronic displacement, the first of these goals can be achieved by investigating the electronic density. To our knowledge the only study doing so is a high-resolution X-ray study of P-stabilized ylides by Yufit and co-workers.³⁰ Com-

paring the experimental data with multipole models and topological analysis of the electron density, they were able to give some direct electronic evidence of negative hyperconjugation in these compounds. In this paper, we will tackle this problem from another point of view by investigating variations in electron density using the electronic Fukui function, a tool from conceptual chemistry. By doing so, we are the first to give clear-cut electronic evidence on the existence of negative hyperconjugation in P-stabilized carbanions.

In a second part of this paper, we use the Natural Bond Orbital (NBO)³¹ method developed by Weinhold and co-workers to estimate the energetic, structural, and electronic impact of the back-bonding interaction. By doing so, we are able to determine to what extent this interaction is responsible for the observed energetic and structural differences between the anionic and neutral compounds.

Computational Details

All structures are optimized at the MP2 as well as DFT (B3LYP) level of theory using a 6-31++G(d,p) basis set for all atoms. All possible conformations have been investigated, and the most stable conformer is retained in all cases. Optimized geometries are provided in the Supporting Information. The energetic data have been completed by MP4/MP2 single-point energies. All calculations have been performed with the Gaussian series of programs.³²

The electronic properties have been studied at the B3LYP level of theory using a Natural Population Analysis (NPA).³¹

Second-order perturbative NBO analysis is used to estimate the metal–ligand back-bonding interaction energy (ΔE_{bb}). The overall energy ΔE_{bb} is obtained by summing up all second-order perturbative interactions (E(2) terms) between the NBO metal donor orbital (carbanion lone pair) and the relevant σ^* P–Y and σ^* P–O acceptor orbital.

The impact of the nature of the σ^* P–Y orbital is studied by considering a series of different functional groups ($\text{Y} = -\text{H}$, $-\text{CH}_3$, $-\text{NH}_2$, $-\text{OH}$, $-\text{F}$) for the anionic CH_2X^- , $\text{C}_2\text{H}_4\text{X}^-$, and allylic $\text{C}_3\text{H}_4\text{X}^-$ compounds.

Results and Discussion

Direct Evidence of Lone Pair/ σ^* Interaction Using Density Differences A direct confirmation of the role of back-bonding can be obtained by a bonding analysis. This latter can be done in several ways, e.g. by analyzing the relevant molecular orbitals. However, one can also consider the entire electron density and its changes upon perturbation to analyze bonding properties. One such function that is looking at changes in electron density upon perturbation is the electronic Fukui function.³³ Although,

(19) El-Nahas, A. M.; Schleyer, P. v. R. *J. Comput. Chem.* **1994**, *15*, 596–626.

(20) Koch, R.; Anders, E. *J. Org. Chem.* **1995**, *60*, 5861–5866.

(21) Kranz, M.; Denmark, S. E. *J. Org. Chem.* **1995**, *60*, 5867–5877.

(22) Kranz, M.; Denmark, S. E.; Swiss, K. A.; Wilson, S. R. *J. Org. Chem.* **1996**, *61*, 8551–8563.

(23) Wetzel, D. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1988**, *110*, 8333–8336.

(24) Bernardi, F.; Schlegel, H. B.; Whangbo, M. H.; Wolfe, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 5633.

(25) Denmark, S. E.; Dorow, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 864–866.

(26) Zarges, W.; Marsch, M.; Harms, K.; Haller, F.; Frenking, G.; Boche, G. *Chem. Ber.* **1991**, *124*, 861–866.

(27) Grutzmacher, H.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 99.

(28) Cramer, C. J.; Denmark, S. E.; Miller, P. C.; Dorow, R. L.; Swiss, K. A.; Wilson, S. R. *J. Am. Chem. Soc.* **1994**, *116*, 2437–2447.

(29) Bansal, R. K.; Gupta, N.; Singh, S.; Karaghiosoff, K.; Mayer, P.; Vogt, M. *Tetrahedron Lett.* **2004**, *45*, 7771–7773.

(30) Yfit, D. S.; Howard, J. A. K.; Davidson, M. G. *J. Chem. Soc., Perkin Trans. 2* **2000**, 249–253.

(31) (a) Weinhold, F.; Landis, C. R. *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective*; Cambridge University Press: 2005. (b) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735. (c) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736. (d) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

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

(33) Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984**, *106*, 4049.

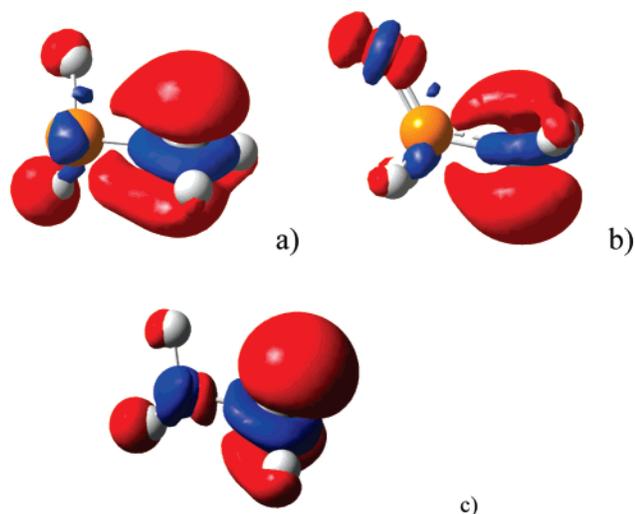


FIGURE 1. B3LYP Fukui function of the CH_2PH_2^- (a), $\text{CH}_2\text{POH}_2^-$ (b), and CH_2NH_2^- (c) molecules (taken at isodensity value of 0.005 e.bohr $^{-3}$) B3LYP/6-31++G(d,p).

mostly used with respect to reactivity, it can also be used to explore bonding, and more specifically back-bonding interactions.³⁴ The Fukui function was introduced in the context of density functional theory by Parr and Yang in 1984 and corresponds to the derivative of the electron density with respect to the number of electrons. In practice, this function usually needs to be approximated as finite-difference terms corresponding to removing (f^-) or adding (f^+ , not considered here) a whole electron.

$$f^-(r) = \left[\frac{\partial(\rho(r))}{\partial N} \right]_{v(r)}^- \approx \frac{\rho^- - \rho^0}{N^- - N^0} = \rho^- - \rho^0 \quad (1)$$

In a frozen orbital ansatz, these Fukui functions correspond to the density of the HOMO (or, for f^+ , of the LUMO), thereby showing their close relation to Fukui's original ideas about frontier MO reactivity. However, the frozen orbital approach is by no means necessary, and it is possible to compute the density difference while taking into consideration the relaxation of all orbitals upon ionization. By including the latter effect, the Fukui function describes bonding more completely than frontier orbital densities, which are only one of its components. In addition, the finite difference Fukui function is a physical observable, whereas frontier orbitals are only mathematical constructs.

Figure 1 shows the Fukui function for the CH_2PH_2^- and $\text{CH}_2\text{POH}_2^-$ as well as for the CH_2NH_2^- molecules. As expected, red zones corresponding to a loss in electron density predominate. These zones indicate that ionization formally occurs out of the carbon lone pair. However, some regions of increased electron density are also found. These regions, shown in blue, are mostly located along the internuclear axis and can be attributed to the polarization along the σ bonds.

Of most interest in the present context are the losses in electron density due to a decrease in back-bonding. These losses are clearly seen in the region corresponding to the π -accepting σ^* P–H and P–O orbitals. However, in Figure 1c, no such change is seen in the region of the N–H σ^* bonds. This remains true even upon plotting the Fukui function with a lower isodensity value. This marked difference is entirely consistent

SCHEME 1. Isodesmic Reactions Used to Study the Total Stabilization of Carbanions by Organophosphorus Compounds

Isodesmic Reaction	
1)	$\text{CH}_3\text{X} + \text{CH}_3^- \rightarrow \text{CH}_2\text{X}^- + \text{CH}_4$
2)	$\text{CH}_3\text{X} + \text{C}_2\text{H}_5^- \rightarrow \text{C}_2\text{H}_4\text{X}^- + \text{CH}_4$
3)	$\text{CH}_3\text{X} + \text{C}_3\text{H}_5^- \rightarrow \text{C}_3\text{H}_4\text{X}^- + \text{CH}_4$

TABLE 1. MP4//MP2 and B3LYP Isodesmic Reaction Energies (kcal/mol) of the Reactions Presented in Scheme 1

	1		2		3	
	MP4	B3LYP	MP4	B3LYP	MP4	B3LYP
PH_2	-22.34	-23.16	-27.54	-27.40	-19.61	-18.40
POH_2	-45.65	-44.37	-47.31	-45.39	-32.09	-28.92
PHCH_3	-25.55	-25.18	-29.33	-27.80	-21.43	-19.31
$\text{P}(\text{CH}_3)_2$	-25.66	-24.52	-26.54	-24.88	-21.50	-18.45
$\text{PO}(\text{CH}_3)_2$	-38.91	-36.30	-39.87	-36.38	-30.04	-26.44
PHNH_2	-28.67	-28.43	-31.96	-30.74	-23.27	-20.96
$\text{P}(\text{NH}_2)_2$	-30.91	-28.98	-30.29	-28.13	-22.10	-19.01
$\text{PO}(\text{NH}_2)_2$	-41.66	-39.73	-43.19	-40.69	-32.56	-29.95
PHOH	-39.82	-39.00	-43.66	-41.48	-31.53	-29.06
$\text{P}(\text{OH})_2$	-41.31	-39.50	-42.95	-40.52	-32.09	-28.92
$\text{PO}(\text{OH})_2$	-47.14	-45.69	-48.81	-46.78	-36.77	-33.57
PHF	-50.38	-49.07	-54.82	-52.46	-40.32	-37.74
PF_2	-55.32	-53.98	-59.04	-56.83	-44.38	-41.88
POF_2	-60.68	-60.30	-62.41	-61.60	-49.09	-47.22

with the fact that significant back-bonding occurs toward the $-\text{PY}_2$ and $-\text{POY}_2$ functional groups but that no such interaction is found with the nitrogen containing groups. By using the Fukui function, we are able for the first time to give direct confirmation of the existence of negative hyperconjugation between the carbanion lone pair and the acceptor σ^* P–Y and P–O orbitals of organophosphorus carbanions.

Energetic Impact of the C Lone Pair/ σ^* Back-Bonding Interaction. With the existence of the back-bonding interaction having been established, we now investigate the impact of this type of interaction. The total stabilization of an adjacent carbanion can be estimated studying the isodesmic reactions presented in Scheme 1.

Table 1 shows the MP4//MP2 and B3LYP reaction energies of the reactions presented above. As shown by this table, both methods lead to reaction energies that are of the same size and similar to those found in the earlier surveys.^{19–22} Isodesmic reactions of the same type have been used to investigate neutral organophosphorus compounds, showing little to no interaction between the phosphorus containing functional group and the neutral organic backbone.^{14,15} The important stabilization observed in Table 1 is therefore clearly linked to the presence of the adjacent carbanion.

As mentioned above, these isodesmic reaction energies measure the total stabilization energy, including changes in π , σ , and electrostatic bonding. To specifically quantify the effect of the negative hyperconjugation, NBO analyses were performed on the optimized compounds. This allows for a detailed analysis of the contributing orbitals.

NBO analysis is based on a method for optimally expressing a given wave function into a localized form. The overall density matrix is transformed to give localized natural bonding orbitals (or NBOs) which are centered on one atom (“core” or “lone pair” orbitals), two atoms (“bond” orbitals), or three atoms

(34) Leyssens, T.; Peeters, D.; Orpen, A. G.; Harvey, J. N. *New J. Chem.* **2005**, *29*, 1424–1430.

TABLE 2. B3LYP NBO Second-order Perturbative Estimate of the Total Lone Pair/ σ^* Back-Bonding Interaction ΔE_{bb} (kcal/mol) in the Anionic CH_2X^- , $\text{C}_2\text{H}_4\text{X}^-$, and $\text{C}_3\text{H}_4\text{X}^-$ Compounds

X/R	CH_2^-	C_2H_4^-	C_3H_4^-	X/R	CH_2^-	C_2H_4^-	C_3H_4^-
PH_2	21.66	22.52	15.62	PHOH	36.65	45.98	32.67
POH_2	29.91	30.70	25.12	P(OH)_2	34.38	35.06	27.64
PHCH_3	22.41	22.52	17.10	PO(OH)_2	40.01	36.03	31.32
$\text{P(CH}_3)_2$	23.70	25.42	17.82	PHF	50.58	58.49	43.04
$\text{PO(CH}_3)_2$	24.60	29.34	24.81	PF_2	41.87	45.26	35.65
PHNH_2	30.97	35.58	23.71	POF_2	47.48	47.77	40.20
$\text{P(NH}_2)_2$	39.48	33.88	23.20				
$\text{PO(NH}_2)_2$	39.46	39.44	30.60				

(“delocalized bond over three centers” or “3C-bond” orbitals). The density matrix is first used to define a minimum basis of atomic orbitals, the natural atomic orbitals (or NAOs), and the NBOs are expressed as an expansion of these orbitals. The NBO orbitals are chosen in such a way as to maximize occupancy, so that delocalization effects appear as weak departures from the idealized localized Lewis structure in which all NBOs have occupancies of exactly 2, 1, or 0. The Natural Bond Orbital (NBO)³¹ method developed by Weinhold and co-workers provides an estimate of the energy impact of secondary bonding interactions which act as small perturbations to the total bonding. The energy contribution is derived from interactions between donor and acceptor orbitals.³⁵ Back-bonding energy contributions are obtained from the NBO estimates of the stabilization interactions associated with partial electron donation from the localized NBOs (carbanion lone pair) of the idealized Lewis structure into the empty non-Lewis orbitals (σ^* P–Y and P–O orbitals), that is, with partial departure from the idealized Lewis structure description. As these interactions are only small departures from the idealized Lewis structure they can be estimated within the NBO method using perturbation theory. The stabilization energy $E(2)$ associated with delocalization from a donor orbital i to an acceptor orbital j is given as $E(2) = \Delta E_{ij} = q_i \times F(i,j)^2 / (\epsilon_j - \epsilon_i)$. In this expression, q_i is the donor orbital occupancy, ϵ_i and ϵ_j are the respective orbital energies, and $F(i,j)$ is the off-diagonal Fock matrix element expressed in the NBO basis.

This approach has been applied to a number of chemical problems, yielding chemically satisfying models accounting for effects such as the small energy difference between cis and trans difluoroethene,³⁶ the torsion barrier to rotation in ethane,³⁷ the relative stability of the isomers of the $\text{HOI-H}_2\text{O}$ complexes,³⁸ the properties of X–H bonds in X–H \cdots Y hydrogen bonds³⁹ for a wide range of X and Y groups, and the impact of negative hyperconjugation on the reactivity of complex heterocyclic systems.⁴⁰

Table 2 shows the total ΔE_{bb} LP/ σ^* back-bonding interaction energy for the compounds studied. These values are comparable to those found for the isodesmic reactions (Table 1), clearly showing that the negative hyperconjugation is responsible for the major part of the observed stabilization, by accounting for 50 to 100% of the total interactions.

(35) (a) Kwon, O.; Sevin, F.; Mckee, M. L. *J. Phys. Chem. A* **2001**, *105*, 913–922. (b) Can, H.; Zhan, D.; Balci, M.; Brickmann, J. *Eur. J. Org. Chem.* **2003**, 68, 1111–1117. (c) Monajjemi, M.; Chahkandi, B. *THEOCHEM* **2005**, *714*, 43–60.

(36) See, e.g., http://www.chem.wisc.edu/~nbo5/tut_del.htm.

(37) Weinhold, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 4188–4194.

(38) Sun, Q.; Li, Z.; Zeng, X.; Ge, M.; Wang, D. *THEOCHEM* **2005**, *724*, 155–161.

(39) Sosa, G. L.; Peruchena, M.; Contreras, R. H.; Castro, E. A. *THEOCHEM* **2002**, *577*, 219–228.

**FIGURE 2.** B3LYP Fukui function of the $\text{C}_3\text{H}_4\text{PF}_2^-$ molecule (taken at isodensity value of 0.005 e.bohr⁻³).

Tables 1 and 2 show the total back-bonding interaction to be influenced by the nature, as well as the formal oxidation state of the P-functional group. Comparing, e.g., the PHY functional groups, we observe an increased stabilization for the more electronegative Y groups (in increasing order $-\text{H} < -\text{CH}_3 < -\text{NH}_2 < -\text{OH} < -\text{F}$). The increased back-bonding for the latter is consistent with the idea of σ^* back-bonding. A very electronegative Y group implies a highly polarized P–Y bond and energetically low σ^* orbital, favoring back-bonding. The more important stabilization by the PY_2 compared to the PHY and the P(V) compared to the P(III) groups is explained by back-bonding interactions toward two σ^* P–Y orbitals for the PY_2 group and a supplementary back-bonding interaction toward the σ^* P–O orbital for the POY_2 group. The less important stabilization of the allylic anions (about 10 kcal/mol less important compared to the stabilization of the methyl and ethyl anions) can be explained by a lone pair that is delocalized over the three carbon centers and therefore less available for back-bonding toward the P-containing functional group. The non-negligible participation of the γ carbon atom to the Fukui function of the $\text{C}_3\text{H}_4\text{PF}_2^-$ molecule, as shown in Figure 2, confirms this three center delocalization.

Electronic Impact of the Carbon Lone pair/ σ^* Back-Bonding Interaction. The NBO analyses also allow for an estimation of the electronic impact of the negative hyperconjugation. This is achieved by deleting specific off-diagonal NBO Fock matrix elements and rediagonalizing this matrix, hereby obtaining a new energy $E(\text{del})$ as well as new density matrix and, hence, modified occupations of the NBO orbitals. The changes in NBO orbital occupation can be directly related to the deleted interaction. Deletion of the LP/ σ^* P–Y and P–O interactions measures the electronic impact of the latter. Table 3 shows the most important changes in occupation number of the NBO orbitals after deletion of these interactions.

As expected deletion of the back-bonding interactions leads to an electronic shift from the σ^* orbitals to the carbanion lone pair (or the carbon lone pair and π^* C–C orbital for the allylic compounds).

The analysis shows the back-bonding interaction to be responsible for an electronic shift of between 0.12 and 0.42 e⁻ (between 0.11 and 0.30e⁻ for the allylic compounds). This analysis furthermore confirms the less important back-bonding interaction observed for the allylic compounds. For the latter, part of the electronic population lost in the σ^* orbitals upon deletion of the back-bonding interaction is recovered in the π^* C–C orbital, again showing the delocalization of the lone pair over the three carbon centers.

The important electronic shift associated with the back-bonding interaction leads to slightly negatively (positively for the allylic carbanions) charged functional groups, contrary to

(40) Lill, S. O. N.; Rauhut, G.; Anders, E. *Chem.–Eur. J.* **2003**, *9*, 3143.

TABLE 3. Change in Occupation Number of the NBO Orbitals (Lone Pair, σ^* P–Y and P–O Orbitals, and π^* C–C Orbital) after Deletion of the Lone Pair/ σ^* Orbital Interactions (B3LYP)

X/R	CH ₂ [−]		C ₂ H ₄ [−]		C ₃ H ₄ [−]		π^* C–C
	σ^*	LP	σ^*	LP	σ^*	LP	
PH ₂	−0.21	0.23	−0.22	0.21	−0.15	0.07	0.08
POH ₂	−0.18	0.21	−0.20	0.20	−0.14	0.05	0.12
PHCH ₃	−0.21	0.24	−0.22	0.22	−0.15	0.08	0.09
P(CH ₃) ₂	−0.20	0.22	−0.22	0.22	−0.15	0.07	0.09
PO(CH ₃) ₂	−0.12	0.10	−0.15	0.13	−0.11	0.01	0.11
PHNH ₂	−0.24	0.28	−0.29	0.30	−0.17	0.07	0.13
P(NH ₂) ₂	−0.26	0.26	−0.27	0.28	−0.17	0.08	0.11
PO(NH ₂) ₂	−0.17	0.19	−0.20	0.21	−0.14	0.04	0.12
PHOH	−0.28	0.27	−0.36	0.38	−0.26	0.13	0.14
P(OH) ₂	−0.27	0.30	−0.30	0.30	−0.21	0.11	0.13
PO(OH) ₂	−0.15	0.21	−0.20	0.21	−0.12	0.06	0.11
PHF	−0.37	0.39	−0.42	0.40	−0.30	0.15	0.16
PF ₂	−0.32	0.38	−0.35	0.37	−0.27	0.14	0.16
POF ₂	−0.17	0.26	−0.18	0.24	−0.15	0.08	0.12

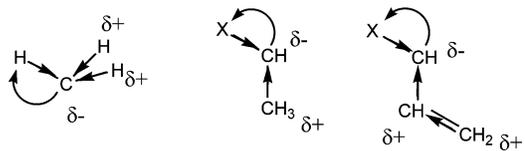
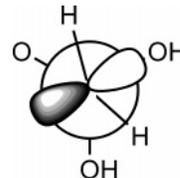
TABLE 4. B3LYP NBO Charge of the Functional Group for the Neutral CH₃X and Anionic CH₂X[−], C₂H₄X[−], and C₃H₄X[−] Compounds, as well as the NBO* Charge of the Anionic Compounds Obtained after Deletion of All σ^* P–Y/LP and All σ^* P–O/LP Back-Bonding Interactions

X/R	NBO		NBO		NBO*		
	CH ₃	CH ₂ [−]	C ₂ H ₄ [−]	C ₃ H ₄ [−]	CH ₂ [−]	C ₂ H ₄ [−]	C ₃ H ₄ [−]
PH ₂	0.23	−0.08	−0.07	0.05	0.13	0.15	0.20
POH ₂	0.26	−0.06	−0.04	0.05	0.12	0.16	0.19
PHCH ₃	0.25	−0.10	−0.09	0.03	0.11	0.13	0.18
P(CH ₃) ₂	0.26	−0.06	−0.06	0.05	0.14	0.16	0.20
PO(CH ₃) ₂	0.28	−0.02	−0.00	0.09	0.10	0.15	0.20
PHNH ₂	0.27	−0.12	−0.13	0.01	0.12	0.16	0.18
P(NH ₂) ₂	0.28	−0.06	−0.06	0.06	0.20	0.21	0.23
PO(NH ₂) ₂	0.29	−0.03	−0.02	0.08	0.14	0.18	0.22
PHOH	0.26	−0.11	−0.15	−0.03	0.17	0.21	0.23
P(OH) ₂	0.27	−0.07	−0.07	0.05	0.20	0.23	0.26
PO(OH) ₂	0.26	−0.03	−0.02	0.06	0.12	0.18	0.18
PHF	0.27	−0.18	−0.18	−0.06	0.19	0.24	0.24
PF ₂	0.30	−0.13	−0.13	−0.01	0.19	0.22	0.26
POF ₂	0.26	−0.06	−0.05	0.03	0.11	0.13	0.18

the positive polarization of these groups in the neutral compounds (Table 4). As shown by Table 4, after deletion of the back-bonding interaction, the functional groups in the anionic compounds recover a positive charge comparable to that observed for the neutral compounds and consistent with a σ donating effect of about 0.2/0.3 e[−] in agreement with the highly electropositive character of these groups.^{41,42} From this analysis it is clear that the phosphorus containing functional groups studied in this paper should be described as σ donor/ π acceptor functional groups.

As for the neutral compounds,^{14,15} the important positive charge on the phosphorus atom polarizes all σ C–H, σ C–C, and π C–C bonds of the organic backbone toward the substituted carbon atom, leading to a total polarization as presented in Figure 3.

Structural Consequences of the Carbon Lone Pair/ σ^* Back-Bonding Interaction. The optimized structural characteristics of the studied anionic compounds are in agreement with those of the earlier surveys. All structures are characterized by

**FIGURE 3.** Polarization of the electron distribution (arrows) as well as increased (δ^+) or decreased (δ^-) charge of the CH, CH₂, and CH₃ parts of the CH₂X[−], C₂H₄X[−], and C₃H₄X[−] anions with respect to the reference molecules (X = −H).**FIGURE 4.** Newman projection of the CH₂PO(OH)₂[−] molecule.

a carbon lone pair eclipsing one of the P–Y or P–O bonds, as shown in the Newman projection for the CH₂PO(OH)₂[−] molecule (Figure 4).

Most striking are the differences in structure with respect to the corresponding neutral compounds. Table 5 shows shorter P–C bonds of at least 0.1 Å for the anionic compounds as well as longer P–Y (P–O) bond lengths and wider Y–P–Y angles. Back-bonding from the lone pair to the σ^* orbitals is thought to be at the origin of these structural changes, as they can be qualitatively attributed to an increased σ^* P–Y (P–O) population.^{43,44}

In order to show that these structural changes are indeed a consequence of the back-bonding interaction, we qualitatively determine what the optimal geometry would be in the absence of this interaction. This can be achieved by reoptimizing the geometry with the $\sigma^*/$ lone pair interaction deleted. In other words, one looks for an equilibrium structure on the NBO $E(\text{del})$ surface, which differs from the $E(\text{full})$ surface by deletion of all lone pair/ σ^* P–Y and P–O interactions. This type of analysis has recently been used to show the decrease in C–C and increase in metal–ligand bond length for metal–olefin complexes upon deletion of the metal d/π^* C–C back-bonding interaction.⁴⁵ The results obtained using this analysis are also shown in Table 5 for the RPY₂ and RPOY₂ compounds.

As shown in this table, the optimal geometries in the absence of the back-bonding interaction are characterized by longer P–C bonds, shorter P–Y bonds, and sharper Y–P–Y angles for the anionic compounds. The variations between the geometries optimized on the $E(\text{full})$ surface and those optimized on the $E(\text{del})$ surface are comparable to the variations found between the neutral and anionic compounds. Although the structural features of compounds optimized on the $E(\text{del})$ surface resemble those of the neutral molecule, no perfect agreement can be expected due to the presence of an additional hydrogen for the latter. From this analysis it becomes clear that the back-bonding interaction is indeed responsible for the major structural differences observed between the neutral and anionic organophosphorus compounds.

(41) Leyssens, T.; Geerlings, P.; Peeters, D. *J. Phys. Chem. A* **2005**, *109*, 9882–9889.

(42) Leyssens, T.; Geerlings, P.; Peeters, D. *J. Phys. Chem. A* **2006**, *110*, 8872–8879.

(43) Orpen, A. G.; Connelly, N. G. *J. Chem. Soc., Chem. Commun.* **1985**, 1310.

(44) Orpen, A. G.; Connelly, N. G. *Organometallics* **1990**, *9*, 1206.

(45) Kim, K. C.; Lee, K. A.; Kim, C. K.; Lee, B. S.; Lee, H. W. *Chem. Phys. Lett.* **2004**, *391*, 321–324.

TABLE 5. Optimal P–C and P–Y^a Bond Lengths (Å) and Y–P–Y Valence Angle (deg) of the RPY₂ and RPOY₂ Compounds^b (R = –CH₂–, –CH₃), as well as These Elements for the Equilibrium Structure of CH₂X[–] on the E(del) Surface

X/R	P–C			P–Y			Y–P–Y		
	CH ₃	CH ₂ [–]	CH ₂ ^{–*}	CH ₃	CH ₂ [–]	CH ₂ ^{–*}	CH ₃	CH ₂ [–]	CH ₂ ^{–*}
PH ₂	1.88	1.76	1.94	1.42	1.49	1.44	93.4	89.1	104.3
POH ₂	1.82	1.73	1.84	1.42	1.43	1.43	101.0	100.4	105.1
P(CH ₃) ₂	1.87	1.74	1.87	1.87	1.92	1.87	99.4	93.4	98.1
PO(CH ₃) ₂	1.83	1.74	1.87	1.83	1.86	1.82	104.8	102.8	104.8
P(NH ₂) ₂	1.85	1.73	1.85	1.73	1.83	1.75	110.5	88.2	108.7
PO(NH ₂) ₂	1.83	1.71	1.88	1.69	1.78	1.71	99.2	93.8	97.6
P(OH) ₂	1.84	1.72	1.81	1.68	1.75	1.70	103.2	88.5	103.3
PF ₂	1.84	1.69	1.82	1.64	1.73	1.65	98.1	86.8	97.7
POF ₂	1.80	1.67	1.70	1.59	1.66	1.62	98.4	90.3	99.6

^a The data is given for the P–Y bond eclipsing the lone pair. ^b The very flat potential energy surfaces observed for X = –PO(OH)₂ due to the rotation of the –OH bonds make it difficult to locate a minimum for this case.

Conclusion

Compelling electronic evidence is given on the existence of a lone pair/ σ^* P–Y (P–O) back-donating interaction. This has been achieved by the analysis of the calculated electron density and of the changes in density upon ionization, the finite difference Fukui function.

The qualitative as well as quantitative energetic, electronic, and structural effects of this interaction are investigated using different types of NBO analyses. A second-order perturbation energy analysis of the negative hyperconjugation interaction confirms the latter to be responsible for the important stabilization of carbanions by phosphorus containing compounds. This stabilization is furthermore shown to depend on the nature of the P–Y bond and can mount up to 60 kcal/mol. The changes in electronic population of the NBO orbitals upon deletion of the back-bonding interaction not only shows an important electronic π shift from the lone pair to the σ^* orbitals but also furthermore leads to a σ -donating effect for these groups in agreement with their low electronegativity value. The phosphorus containing functional groups studied here should there-

fore be seen as σ donor/ π acceptor groups. In a final NBO analysis, we reoptimized the anions without taking the back-bonding interaction into account, clearly showing for the first time that this interaction is indeed responsible for the observed structural differences between the anionic and neutral organophosphorus compounds.

Acknowledgment. The author is indebted to the Belgian National Fund for Scientific Research (F.N.R.S.) for its financial support to this research (Tom Leyskens is a Postdoctoral Research Fellow). He would like also to thank the F.N.R.S. for its support in the access of computational facilities (FRFC project N°2.4556.99 “Simulations numériques et traitement des données”).

Supporting Information Available: Optimized structures (at B3LYP and MP2 level of theory) of all compounds studied (given as z -matrices). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO7025756