CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200802307

The Ever-Surprising Chemistry of Boron: Enhanced Acidity of Phosphine•Boranes

Marcela Hurtado,[a] Manuel Yánez,*[a] Rebeca Herrero,[b] Andrés Guerrero,[b] Juan Z. Dávalos,[b] José-Luis M. Abboud,*[b] Brahim Khater,[c] and Jean-Claude Guillemin*[c]

Abstract: The gas-phase acidity of a series of phosphines and their corresponding phosphine•borane derivatives was measured by FT-ICR techniques. BH_3 attachment leads to a substantial increase of the intrinsic acidity of the system (from 80 to 110 $kJ\,mol^{-1}$). This acidity-enhancing effect of BH_3 is enormous, between 13 and 18 orders of magnitude in terms of ionization constants. This indicates that the enhancement of the acidity of protic acids by Lewis acids usually observed in solution also occurs in the gas phase. High-level DFT calculations reveal that this acidity enhancement is essentially due to stronger stabilization of the anion with respect to the neutral species on BH_3 association, due to a stronger electron donor ability of P in the anion and better dispersion of the negative charge in the system when the BH_3 group is present. Our study also shows that deprotonation of $ClCH_2PH_2$ and $ClCH_2PH_2{\cdot}BH_3$ is followed by chloride departure. For the latter compound deprotonation at the BH_3 group is found to be more favorable than PH_2 deprotonation, and the subsequent loss of Cl^- is kinetically favored with respect to loss of Cl^- in a typical S_N2 process. Hence, $ClCH_2PH_2{\cdot}BH_3$ is the only phosphine•borane adduct included in this study which behaves as a boron acid rather than as a phosphorus acid.

Keywords: ab initio calculations • acidity • gas-phase reactions • ion cyclotron resonance • phosphanes

Introduction

Phosphine•boranes are formed by the association of a phosphine and a borane, whereby the properties of both the free phosphine and the free borane are completely modified. Thus, phosphine•boranes are much less volatile than the corresponding free compounds and not at all pyrophoric, and many other of their physicochemical properties are also different.[1]

The development of gas-phase ion chemistry in the last decades of the 1900s led to a significant change in our view of chemical reactivity. The absence of solute–solvent and counterion interactions revealed the existence of reactivity trends which were very different to those usually accepted and obtained in condensed media. One point of interest was whether a result observed in the condensed phase carries over to the gas phase, that is, is an intrinsic effect or a solvent effect. As a consequence, a great deal of effort was concentrated on determining intrinsic reactivities, in particular intrinsic basicities and acidities.[2–5]

The gas-phase acidity of phosphines has been reported[6,7] and the role played by the substituent on the acidity of the molecule clearly evidenced. In particular the presence of an α,β-unsaturated substituent[6] with or without an electron-withdrawing group[5,7] led to a huge increase in acidity.

The gas-phase acidity of boranes has also attracted some attention.[8,9] In recent studies[9] it was concluded that, although carbon is more electronegative than boron, BH_3 is a

---

[a] Dr. M. Hurtado, Prof. Dr. M. Yánez
Departamento de Química, C-9
Universidad Autónoma de Madrid
Cantoblanco, 28049 Madrid (Spain)
Fax: (+34) 91-497-5238
E-mail: manuel.yanez@uam.es

[b] R. Herrero, A. Guerrero, Dr. J. Z. Dávalos,
Prof. Dr. J.-L. M. Abboud
Instituto de Química Física Rocasolano, CSIC
C/Serrano, 119. 28006 Madrid (Spain)
E-mail: iqrla78@iqfr.csic.es

[c] Dr. B. Khater, Dr. J.-C. Guillemin
Sciences Chimiques de Rennes, UMR 6226 CNRS-ENSCR
Avenue du Général Leclerc, 35708 Rennes Cedex 07 (France)
Fax : (+33) 223-23-81-08
E-mail: jean-claude.guillemin@ensc-rennes.fr

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200802307.

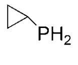
slightly stronger acid than methane, reflecting the fact that the electron affinity of the BH_2 radical is greater than that of the methyl radical.[9] Quite unexpectedly, for boron a dramatic increase in acidity occurs on methyl substitution, and methylborane is predicted to have an intrinsic acidity almost 200 $kJ\,mol^{-1}$ larger than that of BH_3, but also much larger than that of methane, in spite of being a carbon acid. This acidity enhancement reflects the large reinforcement of the C−B bond, which on deprotonation becomes a double bond through donation of the lone pair created on the carbon atom into the empty p orbital on boron. For the same reason, saturated and α,β-unsaturated boranes are much stronger acids than the corresponding hydrocarbons, in spite of also being carbon acids.[9]

The formation of a complex between a primary phosphine and borane will completely change the acidity of the hydrogen atoms on the phosphorus and boron atoms. Moreover the role of the substituent could be completely changed by the presence of the boron compound in the molecule. Thus, ten years ago, the gas-phase negative-ion chemistry of a tertiary phosphine•borane was investigated[10] and, in the absence of hydrogen atoms on the phosphorus atom, $Me_3P{\bullet}BH_3$ was found to be a stronger acid than BH_3, by 712 $kJ\,mol^{-1}$. In the gas phase, the Lewis acid behavior of trimethylborane towards anions has long been known,[11] and addition of alkoxide anions to borate esters has been reported.[12]

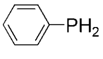
The aim of this paper is to investigate the intrinsic acidity of a suitable set of primary phosphine•boranes by means of Fourier transform ion cyclotron resonance (FT-ICR) spectroscopy[13–17] and DFT calculations, to rationalize the role played by complexation in the acidity of the complex. Five phosphines **1**–**5** and the corresponding phosphine•boranes **6**–**10** were selected for this study on the basis of molecular diversity. Methyl derivatives **1** and **6** are examples of alkyl systems, and phenyl derivatives **3** and **8** of aryl compounds. Cyclopropyl derivatives **2** and **7** and benzyl derivatives **4** and **9** were selected for the potential interaction between the rings and the C−P bond. Chloromethylphosphine **5** and its borane complex **10** were chosen as compounds bearing a chlorine atom, the former being a precursor of the simplest phosphaalkene ($H_2C{=}PH$) under basic conditions.[18]

CH_3PH_2

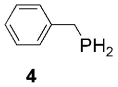
1



2



3



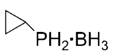
4

$ClCH_2PH_2$

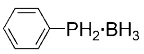
5

$CH_3PH_2{\cdot}BH_3$

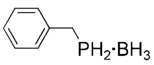
6



7



8



9

$ClCH_2PH_2{\cdot}BH_3$

10

Experimental Section

Caution: Phosphines and phosphine•boranes are malodorous and potentially toxic compounds. All reactions and handling should be carried out under a well-ventilated hood.

Materials: Lithium aluminum hydride, aluminum trichloride, bromocyclopropane, dichlorophenylphosphine, diethyl methylphosphonate, diethyl benzylphosphonate, chloromethylphosphonic acid dichloride, diethyl chlorophosphate, borane•tetrahydrofuran complex solution, and tetraethylene glycol dimethyl ether (tetraglyme) were purchased from Aldrich. All experiments at atmospheric pressure were performed under nitrogen.

General: ^{1}H (400 MHz), ^{13}C (100 MHz), ^{31}P (162 MHz), and ^{11}B (128.4 MHz) NMR spectra were recorded on a Bruker ARX400 spectrometer. Chemical shifts are given in parts per million (δ) relative to tetramethylsilane (^{1}H), solvent (^{13}C, $\delta(CDCl_3)=77.0$ ppm), external 85% H_3PO_4 (^{31}P NMR), and external $BF_3{\cdot}Et_2O$ (^{11}B NMR). The NMR spectra were recorded in $CDCl_3$. High-resolution mass spectrometry (HRMS) was performed on a Varian MAT 311 instrument.

Preparation of 1–10: Phosphine•boranes **6**–**10** were prepared starting from free phosphines **1**–**5**. The preparation of methylphosphine (**1**),[19] phenylphosphine (**3**),[20] benzylphosphine (**4**),[20] chloromethylphosphine (**5**),[21] methylphosphine•borane (**6**),[22] phenylphosphine•borane (**8**),[22] and diborane[23] has already been reported, but several synthesis were partially modified in this work. Cyclopropylphosphine (**2**)[24] was prepared by reduction of the corresponding diethyl cyclopropylphosphonate **11**. Experimental procedures for **1**–**6**, **8**, and **11** are given in the Supporting Information.

Cyclopropyl- (7) and chloromethylphosphine•borane (10): A solution of $BH_3{\cdot}$thf or $BH_3{\cdot}Me_2S$ (5 mL, 1 M, 5 mmol) was slowly added to a previously frozen (−196°C) solution of phosphine **2** or **5** (5 mmol) in dry dichloromethane (5 mL). The reaction mixture was allowed to warm to room temperature and was stirred for 5 min at this temperature. The mixture was then distilled off on a vacuum line and the corresponding phosphine•borane **7** or **10** was selectively condensed in a trap cooled to −40°C (0.1 mmHg). This cell was then disconnected from the vacuum line by stopcocks and attached to the mass spectrometer. **7**: Yield: 95% (based on the free phosphine). ^{1}H NMR ($CDCl_3$, 25°C): $\delta=0.25$ (qt, $^{1}J(B,H)=98.8$ Hz, $^{3}J(H,H)=7.5$ Hz, 3H, BH_3), 0.70–0.97 (m, 5H, cyclopropyl), 4.78 ppm (dq, $^{2}J(H,P)=370$ Hz, $^{3}J(H,H)=7.5$ Hz, 2H, PH_2); ^{31}P NMR ($CDCl_3$, 25°C): $\delta=-43.2$ ppm (q, $^{1}J(P,B)=43.3$ Hz); ^{13}C NMR ($CDCl_3$, 25°C): $\delta=-5.9$ ($^{1}J(C,H)=170.1$ Hz (t), $^{1}J(C,P)=58.1$ Hz (d), CH_2), 3.2 ppm ($^{1}J(C,H)=167.6$ Hz (d), $^{2}J(C,P)=2.2$ Hz (d), CH); ^{11}B NMR ($CDCl_3$, 25°C): $\delta=-45$ ppm; IR (film, 77 K): $\tilde{\nu}=1045$ (s), 1420 (s), 2348 (s, ν_{BH}), 2398 (s, ν_{PH}), 2959 (s), 3088 cm^{-1} (w); HRMS calcd for $C_3H_{10}BP^{+}$: 88.0613; found: 88.062. **10**: Yield: 93% (based on the free phosphine). ^{1}H NMR ($CDCl_3$, 25°C): $\delta=0.20$–1.10 (q, $^{1}J(B,H)=98.2$ Hz, $^{3}J(H,H)=7.1$ Hz, 3H, BH_3), 3.76 (m, $^{3}J(H,H)=6.0$ Hz, $^{2}J(P,H)=8.0$ Hz, 2H, CH_2), 5.01 ppm (dtq, $^{1}J_{PH}=380$ Hz, $^{3}J(H,H)=7.1$ Hz, 6.0 Hz, 2H, PH_2); ^{31}P NMR ($CDCl_3$, 25°C): $\delta=-28.5$ ppm (tq, $^{1}J(B,P)=34.9$ Hz); ^{13}C NMR ($CDCl_3$, 25°C): $\delta=28.0$ ppm ($^{1}J(C,P)=31.2$ Hz (d), $^{1}J(C,H)=153.4$ Hz (t), CH_2); ^{11}B NMR ($CDCl_3$, 25°C): $\delta=-42.6$ ppm; IR (film, 77 K): $\tilde{\nu}=871$ (s, ν_{CCl}), 1470 (m), 2349 (m, ν_{BH}), 2396 (s, ν_{PH}), 2846 (w), 2915 (s), 2963 cm^{-1} (w); HRMS calcd for $CH_7{}^{11}B^{35}ClP^{+}$: 96.0067; found: 96.007.

Benzylphosphine•borane (9): A solution of $BH_3{\cdot}$thf or $BH_3{\cdot}Me_2S$ (6 mL of 1 M sol., 6 mmol) was slowly added to a previously frozen (−196°C) solution of phosphine **4** (5 mmol) in dry dichloromethane (5 mL). The reaction mixture was allowed to warm to room temperature and stirred for 20 min at this temperature. The low-boiling compounds were then removed in vacuo and the crude mixture was directly used without further purification. Attempts to purify the crude compound by distillation on a vacuum line (0.1 mmHg) led to a 2:1 mixture of compounds **4**:**9.** Yield: 95% (crude and based on the free phosphine). ^{1}H NMR ($CDCl_3$, 25°C): $\delta=0.60$ (qt, $^{1}J(B,H)=98.6$ Hz, $^{3}J(H,H)=7.3$ Hz, 3H, BH_3), 2.96 (dt, $^{3}J(H,H)=6.6$ Hz, $^{2}J(P,H)=10.5$ Hz, 2H, CH_2), 4.46 (dsext., $^{1}J(P,H)=366.5$ Hz, $^{3}J(H,H)=6.6$ Hz, 6.6 Hz, 2H, PH_2), 7.10 ppm (m, 5H, Ph); ^{31}P NMR ($CDCl_3$, 25°C): $\delta=-39.4$ ppm (qt, $^{1}J(P,B)=32.7$ Hz); ^{13}C NMR ($CDCl_3$, 25°C): $\delta=23.5$ ($^{1}J(C,H)=131.9$ Hz (t), $^{1}J(C,P)=33.0$ Hz (d), CH_2), 126.7 ($^{1}J(C,H)=161.4$ Hz (d), $^{5}J(C,P)=3.9$ Hz (d), CH), 128.0 ($^{1}J(C,H)=159.2$ Hz (d), $^{3}J(C,P)=5.1$ Hz, CH), 128.5 ($^{1}J(C,H)=159.9$ Hz (d), $^{4}J(C,P)=2.2$ Hz, CH), 134.1 ppm ($^{2}J(C,P)=9.4$ Hz (d), C); ^{11}B NMR ($CDCl_3$, 25°C): $\delta=-41.7$ ppm; IR (film, 77 K): $\tilde{\nu}=1052$ (s), 1495 (s), 1600 (w, $\nu_{C=C}$), 2358 (s, ν_{BH}), 2398 (s, ν_{PH}), 3029 (m, ν_{CH}), 3231 cm^{-1} (s); HRMS calcd for $C_7H_{12}{}^{11}BP^+$: 138.0770, found: 138.077.

FT-ICR spectrometry: A modified Bruker CMS 47 FT-ICR mass spectrometer was used. A detailed description of the original instrument is given in reference [10]. It has already been used in a number of recent studies.[25–27] Some salient features are as follows: the spectrometer is linked to an Omega Data Station (IonSpec, CA), high vacuum is provided by a Varian TURBO V550 turbomolecular pump (550 $L\,s^{-1}$), and the magnetic field strength of the superconducting magnet is 4.7 T.

Determination of gas-phase acidities (GA): The GA value of a protic acid AH, GA(AH), is the standard Gibbs energy change for reaction (1), $\Delta_r G^0_m(1)$.[28]

$$HA(g) \rightarrow H^+(g) + A^-(g) \quad \Delta_r G^0_m(1) \tag{1}$$

Gaseous mixtures of the phosphine RPH_2 (or the adduct $RPH_2{\cdot}BH_3$) and a reference acid $A_{ref}H$ of known gas-phase acidity were introduced into the high-vacuum section of the instrument. Typical partial pressures were in the range 2×10^{-8} to 1×10^{-7} mbar. The average temperature of the cell was 331 K. Isoamyl nitrite (*iso*-$C_5H_{11}NO_2$) containing about 20% of methanol was added (nominal pressures of $(2–3)\times10^{-8}$ mbar). Resonant capture of electrons (nominal energies of 0.8 eV) by *iso*-$C_5H_{11}NO_2$ and CH_3NO_2 provided a mixture of the anions *iso*-$C_5H_{11}O^-$ and CH_3O^-. If the total pressure was less than 2×10^{-7} mbar, argon was added up to a total pressure on this order. After reaction times of 5–12 s, all *iso*-$C_5H_{11}O^-$ and CH_3O^- were protonated by RPH_2, $RPH_2{\cdot}BH_3$, and/or $A_{ref}H$. In all cases, and whenever the couples $RPH^-/A_{ref}{}^-$ or $(RPH{\cdot}BH_3)^-/A_{ref}{}^-$ coexisted for periods ranging between 30 and 60 s, one of these ions was isolated by means of ion-selection techniques and allowed to react with the neutral species, and the system was monitored for up to 60 s in some cases. In all cases, it was established that reaction (2) had reached a state of equilibrium during this time.

$$RPH_2\cdot BH_3(g) + A_{ref}{}^-(g) \rightarrow (RPH\cdot BH_3)^-(g) + A_{ref}H(g) \quad K_p(2) \quad \Delta_r G^0_m(2) \tag{2}$$

Thus, from experiment to experiment, the limiting ratio of abundances of the two ions remained constant within 5%, irrespective of whether ions $A_{ref}{}^-$, RPH^-, or $(RPH{\cdot}BH_3)^-$ were selected. In other experiments, no selection was carried out, but the ratio was the same, within these limits.

Experimental GA values are determined from $GA(A_{ref}H)$ and $K_p(2)$ through Equation (3).

$$GA(RPBH_5) = GA(A_{ref}H) - RT\ln K_p(2) \tag{3}$$

$K_p(2)$ involves the partial pressures P of the neutral and ionic species taking part in reaction (2) and is given by the product of the two terms in parentheses in Equation (4).

$$K_p(2) = (P_{A_{ref}H}/P_{RPH\cdot BH_3})(P_{RPH\cdot BH_3^-}/P_{A_{ref}^-}) \tag{4}$$

The pressures of the neutral species were measured with a Bayard–Alpert ion gauge. Its readings were corrected according to the method of Bartmess and Georgiadis;[29] full details are given in the Supporting Information. The ratio of the pressures of the ionic species was taken as the ratio of the relevant ion intensities.

It is unfortunate that both adducts partially dissociate in the gas phase, and this phenomenon is more important in the case of the neutral species [reaction (5)].

$$RPH_2\cdot BH_3(g) \rightarrow RPH_2(g) + BH_3(g) \quad K_p(5) \tag{5}$$

Hence, in the absence of a reliable experimental value for $K_p(5)$ it is not possible to accurately determine $K_p(2)$. We thus ignored the effect of reaction (5) and assumed that the experimental readings of pressure correspond to those of pure adducts $RPH_2{\cdot}BH_3(g)$. At least formally, this suggests that the acidities thus determined are upper limits for the true GA values.

Table 1. Experimental and calculated GA values[a] for compounds **1–10**.

R	$GA(RPH_2)$[b]	$GA(RPH_2{\cdot}BH_3)$[c]	$-\delta GA$[d]	$-\Delta_r G_1^{0}$[d]	$-\Delta_r G_4^{0}$[d]
C_6H_5	1457.3 ± 0.8	1375.0 ± 2.5	82.3	*50.8*	*128.8*
	1455.1	*1379.1*	*76.0*		
$C_6H_5CH_2$	1493.8 ± 0.9	1380.4 ± 2.5	113.4	*49.3*	*162.8*
	1495.3	*1382.8*	*115.1*		
c-C_3H_5	1510.0 ± 3.0	1408.9 ± 2.8	101.1	*56.0*	*163.2*
	1507.8	*1402.0*	*105.8*		
CH_3	1530.0 ± 2.5	1411.9 ± 2.3	118.1	*55.7*	*176.2*
	1530.7 (*1528.2*)	*1410.2* (*1404.8*)	*120.5* (*123.4*)		
$ClCH_2$	*1364.3*[e]	*1312.2*[e]	*52.1*		

[a] All values in $kJ\,mol^{-1}$. Calculated values, obtained at the B3LYP/6-311++G(3df,2p) level, are given in italics. Values in parentheses were calculated at the G3X level. [b] Uncertainties taken as twice the absolute deviation. [c] The reported uncertainties do not include those originating from dissociation of the adducts. [d] Defined in the text. [e] These values should be taken as apparent acidities, because they do not correspond strictly speaking to the process defined by Equation (1), since the deprotonation process triggers chloride departure.

Generally, when these problems are absent, the standard deviation for the experimental GA values determined by averaging the results obtained with at least three different references, ranges between 0.8 and 1.2 $kJ\,mol^{-1}$. The values of $GA(RPH_2)$ and $GA(RPBH_5)$, obtained as indicated above, are summarized in Table 1 and full details are given in Tables S1 and S2 in the Supporting Information. While the precision is satisfactory, the accuracy is generally less so, and in the NIST database[28b] the total uncertainty is generally taken as 8.4 $kJ\,mol^{-1}$ to allow for anchoring and other problems (full details are given in the Supporting Information). We believe that this is a conservative estimate in our case.

As discussed in detail below, deprotonation of **5** and **10** is followed by departure of Cl^-, and a true GA cannot be determined. Nevertheless, we monitored the formation of chloride ion as a function of the gas-phase acidity of the reference acids. As the acidity of the latter increases, this becomes increasingly difficult because of the importance of the formation of $[(A_{ref})_2H]^-$ ions (our spectrometer is not fitted with an external ion source). Therefore, although we report below some "limiting" values of the acidities of reference acids leading to the formation of Cl^-, it is clear that these values must be considered with caution and only as reasonable lower limits of the acidities of the corresponding $A_{ref}H$.

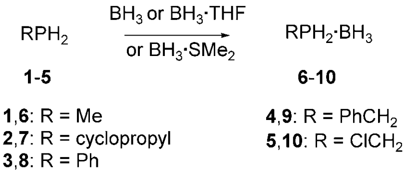
Computational Details

Standard DFT and high-level ab initio calculations on the various systems under study were performed with the Gaussian 03 suite of programs.[30] These systems have three potential acidic sites, namely, CH, BH, and PH bonds. In our survey we considered all possibilities and all possible conformers. In all cases, with the sole exception of $ClCH_2PH_2{\cdot}BH_3$, the most stable anion was obtained by deprotonation of the PH_2 group. For the sake of simplicity, in the discussion which follows we consider exclusively the most stable anion in its most stable conformation. All geometries were optimized at the B3LYP/6-31+G(d,p) level, which usually yields good geometries with low computational demand. Harmonic vibrational frequencies were obtained at the same level of accuracy to assess whether the structures found correspond to local minima of the potential-energy surface and to evaluate the zero-point energy (ZPE) and other thermal corrections. To obtain reliable energies, single-point calculations at the B3LYP/6-311++G(3df,2p) level were carried out. Although the level of theory used has been found to be reliable for the determination of both intrinsic basicities and acidities, we assessed our model by comparing the calculated B3LYP/6-311++G(3df,2p) acidities with those obtained with G3X theory.[31] For this assessment we chose compounds **1** and **6** as suitable model systems. As we discuss below, the differences between the two models are never larger than 4 kJ mol^{-1}, but more importantly, G3X values are not superior to the B3LYP values in comparison with experimental data.

To gain some insight into the electronic structure and bonding of the systems under investigation, we used the theory of atoms in molecules (AIM)[32] and the electron localization function (ELF).[33] In the framework of the former we evaluated the electron density at the different bond critical points (BCP), which will help us to understand the changes which occur on going from the neutral to the anionic compounds. The ELF[33] is a function which becomes large in regions of space where electron pairs, either bonding or lone pairs, are localized. The function is conveniently scaled between [0,1], and thereby maps from the very low (0) to very high (1) electron localization regimes. In this way it is possible to locate electron localization basins defined by isosurfaces corresponding to an ELF value around 0.87. The attraction basins of ELF have been successfully related to key bonding concepts, such as core, valence, and lone-pair regions, while their populations and synaptic orders have been related to bond order. ELF grids and basin integrations were computed with the TopMod package.[34]

Results and Discussion

Syntheses of phosphines **1**–**5** by reduction of the corresponding phosphonates or dichloro phosphines have already been reported.[20–22] Phosphine•boranes **6**–**10** were prepared by addition of BH_3 to free phosphines **1**–**5** (Scheme 1). Pure diborane was used with the volatile derivative (**1**→**6**) and a solution of BH_3•THF or BH_3•Me_2S with phosphines that formed complexes easily separated from solvents by distillation (**7**–**10**). Three new compounds were prepared in this study: cyclopropyl- (**7**), benzyl- (**9**) and chloromethylphosphine•borane (**10**). They were easily characterized by NMR spectroscopy and mass spectrometry. In the ^{31}P NMR spectrum, the downfield chemical shift [$\delta = -28.5$ (**7**), -39.4 (**9**), -42.6 ppm (**10**)] and coupling constant $^1J_{P,H}$ around 380 Hz are characteristic of these compounds.[22,23] The ^{11}B NMR chemical shift of about $\delta = -42$ ppm and observation of the molecular ion by high-resolution mass spectrometry confirm the structures. The optimized geometries of neutral and deprotonated compounds as well as the calculated energies are summarized in Tables S3 and S4 of the Supporting Information, respectively.



Scheme 1.

The experimental values of GA(RPH_2) and GA(RPH_2•BH_3), obtained as indicated above, are given in Table 1, together with the B3LYP/6-311++G(3df,2p) calculated values.

In all cases, the phosphines are significantly less acidic than their BH_3 adducts. This follows from the observation that their corresponding anions RPH^- are fully re-protonated by the neutral adducts. The calculated GA values nicely agree with the experimental results. The agreement between experimental and calculated values is very good, the averaged absolute deviation of 2.7 kJ mol^{-1} being on the same order as the experimental error. The agreement between G3X calculated values and the experimental data is slightly worse than that obtained for DFT values.

Collision-induced decomposition (CID) of $(R\text{-}PBH_4)^-$ (using argon as the target gas) produced by on-resonance (structural assignment) or slightly off resonance (SORI)[35] (lowest energy pathway for decomposition) excitation of these ions (in all cases using the lowest possible energy) cleanly leads to the formation of RPH^- as the sole ionic product. We take this as implying that 1) the acidic proton belongs to the phosphine moiety and, 2) the P–B bond is most likely the weakest bond in these ions. As we discuss below, computational results confirm that in this family of compounds, deprotonation of the PH_2 group is thermodynamically favored over that of BH_3, with the sole exception of $ClCH_2PH_2$•BH_3.

In line with these observations, our calculations show that in all cases, with the sole exception of $ClCH_2PH_2$•BH_3, which will be discussed below, all systems investigated behave as phosphorus acids, and loss of the proton from the BH_3 group or a CH group is 180–250 or 50–150 kJ mol^{-1} less favorable.

Deprotonation of $ClCH_2PH_2$ (**5**) does not lead to the observation of its corresponding anion $(ClCH_2PH)^-$. In all cases, the product of the reaction between $ClCH_2PH_2$ and the anion of the reference acid is chloride ion. This suggests that the behavior in the gas phase is similar to that in solution.[18] Interestingly, this reaction is observed even in the presence of the anion of *p*-hydroxybenzaldehyde, a very strong acid endowed with a rather weak conjugate base in the gas phase (GA = 1364.4 kJ mol^{-1}). This suggests that chloride departure involves an elimination process.[36] This is corroborated by our DFT calculations, which show that deprotonation of the PH_2 group leads to a complex in which a Cl^- ion is weakly bound to one of the H atoms of the methylidenephosphine (see Figure 1). Hence, under experimental conditions, deprotonation of $ClCH_2PH_2$ is indeed followed by chloride departure and the formation of methylidenephosphine. It is worth noting that the apparent acidity calcu-

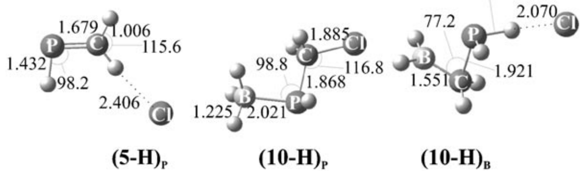
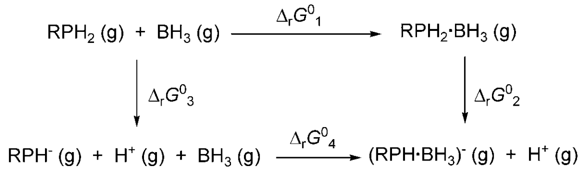


Figure 1. Optimized structures of the deprotonated species of compounds **5** and **10**. Structure **(5-H)**$_P$ is the P-deprotonated species of **5**. Structures **(10-H)**$_P$ and **(10-H)**$_B$ correspond to the P and B deprotonation of compound **10**, respectively. H···Cl distances are in angstrom.

lated for compound **5** is equal to that of *p*-hydroxybenzaldehyde, which defines a lower limit for this magnitude. While this extraordinary agreement is possibly fortuitous, it seems to indicate that Cl^- departure triggered by deprotonation of **5** involves a very low activation barrier. In fact our calculations on the deprotonated species evolve to form **(5-H)$_P$** without an activation barrier.

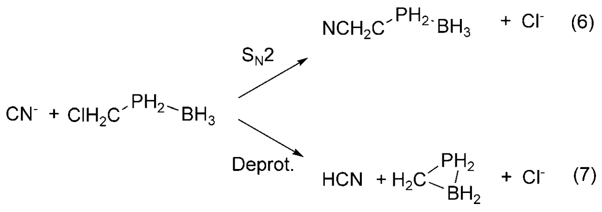
We observed the same behavior for deprotonation of $ClCH_2PH_2{\cdot}BH_3$ (**10**), that is, its anion was not detected under any circumstances. Chloride ion is observed even in the presence of the anion of *o*-toluic acid (GA = 1384.5 kJ mol^{-1}). Again, this suggests the existence of two reactive channels leading to formation of Cl^-.[36] The theoretical survey of the possible deprotonation processes of this compound shows that deprotonation of the PH_2 group is energetically less favorable than deprotonation of the BH_3 group. This theoretical finding agrees with experimental observations which suggest that also in this case deprotonation of the system triggers chloride departure. In fact, as illustrated in Figure 1, in the less stable anion produced by deprotonation of the PH_2 group, the Cl atom remains attached to the carbon atom. Conversely, deprotonation of the BH_3 group involved a drastic internal reorganization of the system, associated with cleavage of the P–B bond and formation of a rather strong C–B bond with non-negligible double-bond character, and cleavage of the C–Cl bond. The consequence of this drastic structural rearrangement is that the most stable anion can be viewed as the interaction between Cl^- and one of the H atoms of the PH_2 group of the neutral $H_2BCH_2PH_2$ moiety (see Figure 1). In this case the calculated apparent acidity of the system (1312.2 kJ mol^{-1}) is significantly different from that of *o*-toluic acid, a rough experimental estimate of the lower limit of the acidity of **10**. This energy difference is likely used to overcome the activation free-energy barrier associated with the geometrical rearrangement indicated above. In this respect, it is important to note that the acidity of compound **10** when it behaves as a P acid to yield anion **(10-H)$_P$** (see Figure 1) of 1358.6 kJ mol^{-1} is much closer to this experimental lower limit. Hence, one may perhaps infer that even though structure **(10-H)$_B$** in Figure 1 is the most stable anion, the deprotonation process takes place at the PH_2 group, and this is eventually followed by a rearrangement connecting **(10-H)$_P$** with **(10-H)$_B$**. This kind of rearrangement, which would imply an H shift from the BH_3 to the PH group. It often occurs via ion/neutral complexes and involves barriers which are below the energy of the separated products, although they are entropically disfavored. We have located the corresponding transition state, which lies quite high in energy (234 kJ mol^{-1} above **(10-H)$_P$**), that is, although **(10-H)$_B$** is the most stable deprotonated form of **10**, it is unreachable under the current experimental conditions. Hence, we may in principle conclude that the ability of these compounds to lose Cl^- indicates that $ClCH_2PH_2{\cdot}BH_3$ is the only phosphine•borane complex included in this study which should behave as a boron acid rather than as a phosphorus acid.

Nevertheless, the observed loss of Cl^- could be the result of a simple S_N2 reaction,[36] which in principle cannot be ruled out. To investigate whether this possibility can compete with the deprotonation process, we studied both mechanisms at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G(d,p) level (see Scheme 2) using the CN^- ion as a suitable model reactant.



Scheme 2.

Our results (see Table S5 of the Supporting Information) indicate that reaction (6) is 80 kJ mol^{-1} more exothermic than reaction (7). This means that the S_N2 nucleophilic substitution is thermodynamically favored over the deprotonation process. This difference becomes much smaller (35 kJ mol^{-1}) in terms of free energy, due to significant differences between the entropy changes occurring in the two reactions, which favor the deprotonation process. This is, however, only part of the relevant information, since it is necessary to know whether the S_N2 reaction is also kinetically favored. To answer this question we also located the transition states of both reactions (see Figure 2).



$\mathbf{TS_{deprot}}$ $\mathbf{TS_{SN2}}$

Figure 2. Structures of the transition states involved in the deprotonation ($\mathbf{TS_{deprot}}$) and the S_N2 reaction ($\mathbf{TS_{SN2}}$) between CN^- and $ClCH_2PH_2{\cdot}BH_3$.

In the TS for the deprotonation process proton transfer from the BH_3 group towards the CN^- ion triggers departure of a Cl^- ion. Similarly, in the TS for the S_N2 reaction, attachment of CN^- leads to departure of Cl^-. The important result, however, is that this TS is estimated to be 45 kJ mol^{-1} higher in energy than that associated with the deprotonation process. This difference becomes even higher (49 kJ mol^{-1}) in terms of free energy. Hence, although the S_N2 reaction leads to products which are more stable than those associated with the deprotonation process, the reaction is much less favorable from a kinetic viewpoint, so in principle it cannot be repudiated that the observed loss of Cl^- is indeed that associated with the deprotonation process rather than with the S_N2 reaction.

As mentioned above, for a given R, $RPH_2{\cdot}BH_3$ is always a stronger acid than RPH_2. Although substantial, the effect is not constant. It appears that while $C_6H_5PH_2$ and its adduct are the most acidic species, the acidity-enhancing effect of BH_3 as measured by δ_RGA is the smallest in the series. The opposite holds in the case of methylphosphine and its adduct. These facts can be analyzed as follows:

Consider thermodynamic cycle I; Equation (8) holds.

$$\Delta_r G_1^0 + \Delta_r G_2^0 - \Delta_r G_3^0 - \Delta_r G_4^0 = 0 \quad (8)$$

Since $\Delta_r G_2^0 = \mathrm{GA}(RPH_2{\cdot}BH_3)$ and $\Delta_r G_3^0 = \mathrm{GA}(RPH_2)$, Equation (9) follows

$$\delta_R \mathrm{GA} = \Delta_r G_4^0 - \Delta_r G_1^0 \quad (9)$$

where δ_RGA is always negative and so are $\Delta_r G_1^0$ and $\Delta_r G_4^0$. The difference between the latter $\Delta_r G^0$ values measures the difference between the "borane basicities" of RPH_2 and RPH^-. In other words, the acidity-enhancing effect of BH_3 increases with increasing strength of the bond between RPH^- and BH_3 (increasing the absolute value of $\Delta_r G_4^0$) and is weakened by a strengthening of the bond between RPH_2 and BH_3 (increasing the absolute value of $\Delta_r G_1^0$). The calculated values for $\Delta_r G_4^0$ and $\Delta_r G_1^0$ clearly show that the first effect dominates, and the anion is always more stabilized by complexation than the neutral species. This is in agreement with the fact that the electron density at the B–P BCP is larger in the anion than in the neutral system. Our calculated values fulfill Equation (9) with an average deviation of 1.2 kJ mol^{-1}. In the series R = Me, $C_6H_5CH_2$, c-C_3H_5, C_6H_5, the possibility of internal charge delocalization by resonance increases in this order.[36–39] This charge delocalization can reduce the availability of the lone pair(s) to yield both $RPH_2{\cdot}BH_3$ and $(RPH{\cdot}BH_3)^-$, and thus reduce the absolute values of $\Delta_r G_1^0$ and $\Delta_r G_4^0$. The results presented in Table 1 show that $\Delta_r G_1^0$ is not very sensitive to substituent effects. Consistently, the differences between the electron densities at the corresponding B–P BCPs are negligibly small. On the other hand, the absolute values of $\Delta_r G_4^0$ are larger and also strongly depend on the resonance interaction between the substituents and the reactive centers. As expected, the absolute values of $\Delta_r G_4^0$ decrease in the order Me > $C_6H_5CH_2$ ≈ c-C_3H_5 > C_6H_5. This is consistent with the antagonic effects of resonance interactions indicated above. The methylene group also efficiently reduces the resonance interaction between the phenyl group and the phosphine moiety. The same trend is observed in the electron densities at the B–P BCP, and accordingly there is a rather good linear correlation between $\Delta_r G_4^0$ and these densities (see Figure 3).

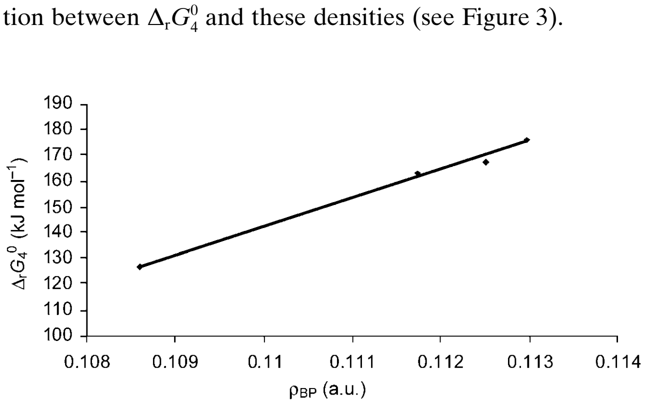


Figure 3. Linear correlation between $\Delta_r G_4^0$ and the electron density at the B–P BCP (ρ_{BP}).

Two factors seem to be responsible for the greater stabilization of the anionic species on association with BH_3. As illustrated in Figure 4, taking **1** and **6** and their corresponding deprotonated forms as suitable model systems, deprotonation of **1**, which changes a P–H bond in the neutral species to a lone pair in the anion, leaves an electron-rich P atom, as reflected in a large population of the corresponding *V*(P) basin. Accordingly the anion behaves as a better electron donor towards the BH_3 moiety. On the other hand, the presence of the BH_3 group contributes to the dispersion of the negative charge of the anionic system, because the hydrogen atoms of this group can easily accumulate a larger net nega-

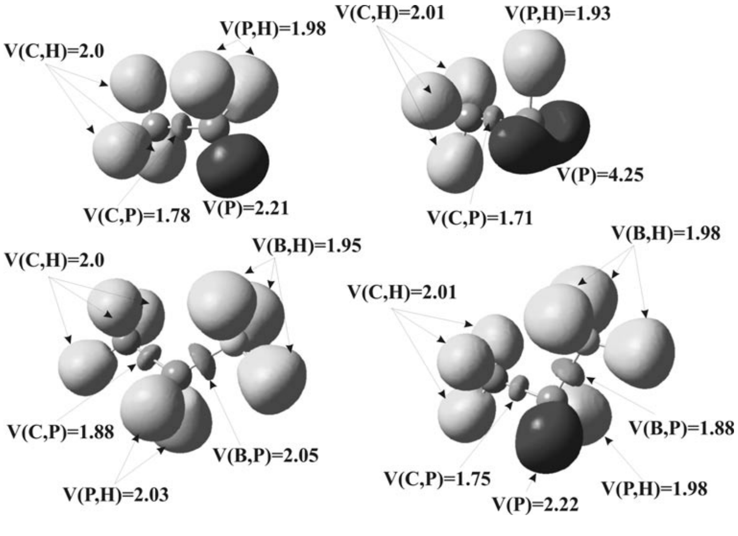


Figure 4. Three-dimensional representations of ELF isosurfaces with ELF = 0.80 for compounds **1** and **6** and their corresponding deprotonated species. Lobes denoted as *V*(C,H), *V*(P,H), *V*(B,H) correspond to basins associated with CH, PH, and BH bonds. Lobes denoted *V*(B,P) correspond to basins associated with B–P bonds. Lobes denoted as *V*(P) correspond to basins associated with P lone pairs. The populations of these basins are also shown.

tive charge, which is apparent when comparing the ELFs of $CH_3PH{\bullet}BH_3^-$ and $CH_3PH_2{\bullet}BH_3$.

This ability of BH_3 to better stabilize anionic species than neutral species is also reflected in the dissociation energies of the P–B bonds. As we mentioned above, B–P bond cleavage in neutral and anionic systems is measured by $\Delta_rG_1^0$ and $\Delta_rG_4^0$, respectively. However, the values reported in Table 1 include relaxation of the two fragments. For instance, the value calculated for $CH_3PH_2{\bullet}BH_3$ implies that the two fragments CH_3PH_2 and BH_3 are in their equilibrium conformation. Although the structural changes of the phosphine on complexation are very small, it is clear that the BH_3 group within the complex is far from being in its equilibrium conformation, since it is strongly pyramidalized. This implies that the dissociation energy, usually defined as the energy difference between the complex and the two subunits at infinite separation, includes the relaxation energy of the BH_3 group, which is significant. Hence, a more realistic estimate of the B–P bond strength would be obtained without allowing relaxation of the fragments.[40] When this is done, the dissociation energies increase by about 50 kJ mol^{-1} for the neutral systems, and by about 85 kJ mol^{-1} for the anions. More importantly, since, as we mentioned above, the geometry distortion undergone by the phosphine moiety is not significant, more than 95 % of this energy increase comes from the relaxation of the BH_3 moiety. In other words, the relaxation energy of the BH_3 moiety, measured as the energy difference between the BH_3 group in the complex and the BH_3 group in its equilibrium geometry, is on the order of 80–89 kJ mol^{-1} when the complex is an anion, and only 51 kJ mol^{-1} for the neutral complex.

Finally, we draw attention to the fact that, in all cases, the acidity-enhancing effect of BH_3 in the systems studied herein, is enormous, between 13 and 18 orders of magnitude in terms of ionization constants.[41] The enhancement of the acidity of protic acids by Lewis acids in solution is known to lead to extremely powerful acidic systems such as magic acid.[42] Here we show that similar situations can be found in the gas phase.

The fact that the calculated GA values for the adducts are in reasonable agreement with the experimental data, implies that the extent of dissociation of $(RPH{\bullet}BH_3)^-(g)$ is relatively small. Consider now the ratio ρ of the pressures of RPH^- and $(RPH{\bullet}BH_3)^-$ ($\rho = P_{RPBH_4^-}/P_{RPH^-}$) It can be readily shown that Equation (10) holds

$$\rho = K_p(10)/P_{BH_3} \tag{10}$$

where $K_p(10)$ pertains to reaction (11). Furthermore, $\Delta_rG_4^0 = -RT\ln K_p(10)$.

$$RPH^-(g) + BH_3(g) \rightarrow (RPH \cdot BH_3)^-(g) \tag{11}$$

The working pressures are in the range of 10^{-11} to 10^{-10} bar. It follows that $K_p(10)$ must be at least one order of magnitude larger than 10^{11}.[43] Hence, the equilibrium constant for the formation of $(RPBH_3)^-$ is at least on the order of 10^{12}. The computed $\Delta_rG_4^0$ values (Table 1) lead to $K_p(10)$ values of at least 10^{20}.

Conclusions

Our experimental and theoretical study on a series of phosphines and their phosphine•borane adducts showed that BH_3 attachment leads to a substantial increase (from 80 to 110 kJ mol^{-1}) in the intrinsic acidity of the system. This acidity-enhancing effect of BH_3 is enormous, between 13 and 18 orders of magnitude in terms of ionization constants. This indicates that the enhancement of the acidity of protic acids by Lewis acids observed in solution[42] also occurs in the gas phase. Density functional theory calculations reveal that this acidity enhancement reflects the greater stabilization of the anion with respect to the neutral species on association with BH_3, due to the greater electron-donor ability of P in the anion and better dispersion of the negative charge within the system when the BH_3 group is present. Our study also shows that deprotonation of $ClCH_2PH_2$ and $ClCH_2PH_2{\bullet}BH_3$ is followed by chloride departure. Although the loss of Cl^- could be also associated with a S_N2 reaction, we have shown that this process is much less favorable from the kinetic viewpoint than the deprotonation reaction. Accordingly, it is reasonable to expect the observed Cl^- departure to be associated with deprotonation of the system, which would imply that $ClCH_2PH_2{\bullet}BH_3$ is the only phosphine•borane adduct included in this study which should behave as a boron acid rather than as a phosphorus acid. Although chloride departure impeded measurement of the acidity of these two compounds, the experimental evidence is consistent with the theoretical analysis.

Acknowledgements

This work has been supported by Grants CTQ 2006-10178/BQU and BQU2003-05827 from Ministerio de Educación y Ciencia (CSIC) , the CNES and PCMI (INSU-CNRS) (ENSCR), by the DGI Project No. BQU2003-00894, Consolider on Molecular Nanoscience, CSD2007-00010, and by the Project MADRISOLAR, Ref.: S-0505/PPQ/0225 of the Comunidad Autónoma de Madrid. A generous allocation of computing time at the CCC of the UAM is also acknowledged.

---

[1] A. C. Gaumont, B. Carboni, *Sci. Synth.* **2004**, *6*, 485–512.
[2] S. G. Lias, J. F. Liebman, R. D. Levin, *J. Phys. Chem. Ref. Data* **1984**, *13*, 695–808.
[3] J. L. M. Abboud, L. Alkorta, P. Burk, J. Z. Davalos, E. Quintanilla, E. W. Della, I. A. Koppel, I. Koppel, *Chem. Phys. Lett.* **2004**, *398*, 560–563; E. Quintanilla, J. Z. Dávalos, J.-L. M. Abboud, M. Alcamí, M. P. Cabildo, R. Claramunt, J. Elguero, O. Mó, M. Yáñez, *Chem. Eur. J.* **2005**, *11*, 1826–1832.
[4] J. P. Kercher, Z. Gengeliczki, B. Sztaray, T. Baer, *J. Phys. Chem. A* **2007**, *111*, 16–26.
[5] J.-C. Guillemin, E. H. Riague, J.-F. Gal, P.-C. Maria, O. Mó, M. Yáñez, *Chem. Eur. J.* **2005**, *11*, 2145–2153.
[6] J.-F. Gal, M. Decouzon, P.-C. Maria, A. I. González, O. Mó, M. Yáñez, S. El Chaouch, J.-C. Guillemin, *J. Am. Chem. Soc.* **2001**, *123*, 6353–6359.

[7] A. Luna, O. Mó, M. Yáñez, J.-F. Gal, P.-C. Maria, J.-C. Guillemin, *Chem. Eur. J.* **2006**, *12*, 9254–9261.
[8] J. E. Bartmess, R. Hinde, *Can. J. Chem.* **2005**, *83*, 2005–2012.
[9] J. A. Gámez, J. C. Guillemin, O. Mó, M. Yáñez, *Chem. Eur. J.* **2008**, *14*, 2201–2208.
[10] J. Ren, D. B. Workman, R. R. Squires, *J. Am. Chem. Soc.* **1998**, *120*, 10511–10522.
[11] M. K. Murphy, J. L. Beauchamp, *J. Am. Chem. Soc.* **1976**, *98*, 1433–1440.
[12] J. P. Kiplinger, C. A. Crowder, D. N. Sorensen, J. E. Bartmess, *J. Am. Soc. Mass Spectrom.* **1994**, *5*, 169–176.
[13] F. H. Laukien, M. Allemann, P. Bischofberger, P. Grossmann, H. P. Kellerhals, P. Kofel in *Fourier Transfrom Mass Spectrometry. Evolution, Innovation and Applications* (Ed.: M. V. Buchanan) ACS, Washington, **1987**.
[14] A. G. Marshall, C. L. Hendrickson, *Int. J. Mass Spectrom.* **2002**, *215*, 59–75.
[15] J.-F. Gal, P.-C. Maria, E. D. Raczynska, *J. Mass Spectrom.* **2001**, *36*, 699–716.
[16] J.-L. M. Abboud, R. Notario in *Nato Science Series C* (Ed.: M. E. Minas da Piedade), Kluwer, Dordrecht, **1999**, p. 281.
[17] A. G. Marshall, C. L. Hendrickson, G. S. Jackson, *Mass Spectrom. Rev.* **1998**, *17*, 1–35.
[18] S. Lacombe, D. Gonbeau, J.-L. Cabioch, B. Pellerin, J.-M. Denis, G. Pfister-Guillouzo, *J. Am. Chem. Soc.* **1988**, *110*, 6964–6967.
[19] K. D. Crosbie, G. M. Sheldrick, *J. Inor. Nucl. Chem.* **1969**, *31*, 3684–3685.
[20] L. Horner, H. Hoffmann, P. Beck, *Chem. Ber.* **1958**, *91*, 1583–1588.
[21] J.-L. Cabioch, B. Pellerin, J.-M. Denis, *Phosph. & Sulfur Silicon Rel. Elem.* **1989**, *44*, 27–32.
[22] K. Bourumeau, A.-C. Gaumont, J.-M. Denis, *J. Organom. Chem.* **1997**, *529*, 205–213.
[23] A. D. Norman, W. L. Jolly, *Inorg. Synth.* **1968**, *11*, 15–19.
[24] L. A. Dinsmore, C. O. Britt, J. E. Boggs, *J. Chem. Phys.* **1971**, *54*, 915–918.
[25] J. Z. Dávalos, R. Herrero, E. Quintanilla, P. Jiménez, J.-F. Gal, P.-C. Maria, J.-L. M. Abboud, *Chem. Eur. J.* **2006**, *12*, 5505–5513.
[26] J. Z. Dávalos, R. Herrero, J.-L. M. Abboud, O. Mó, M. Yáñez, *Angew. Chem.* **2007**, *119*, 385–389; *Angew. Chem. Int. Ed.* **2007**, *46*, 381–385.
[27] R. Herrero, J. Z. Davalos, J.-L. M. Abboud, I. Alkorta, I. Koppel, I. A. Koppel, T. Sonoda, M. Mishima, *Int. J. Mass Spectrom.* **2007**, *267*, 302–307.
[28] a) S. G. Lias, J. E. Bartmess, *Thermochemistry of Ions in the Gas Phase: Gas-Phase Ion Thermochemistry*, NIST Chemistry WeBook, NIST Standard Reference Database Number 69 (Eds.: P. J. Linstrom, W. G. Mallard), **2005**, Institute of Standards and Technology, Gaithersburg MD, 20899, ; b) J. E. Bartmess, *Negative Ion Energetics Data* in NIST Standard References Database Number 69 (Eds.: P. J. Linstrom, W. G. Mallard), **2003**, Institute of Standards and Technology, Gaithersburg MD, 20899, (http://webbook.nist.gov).
[29] J. E. Bartmess, R. M. Georgiadis, *Vacuum* **1983**, *33*, 149–153.
[30] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2003**
[31] L. A. Curtiss, P. C. Redfern, K. Raghavachari, J. A. Pople, *J. Chem. Phys.* **2001**, *114*, 108–117.
[32] R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendon Press, Oxford, **1990**.
[33] A. D. Becke, K. E. Edgecombe, *J. Chem. Phys.* **1990**, *92*, 5397–5403.
[34] S. Noury, X. Krokidis, F. Fuster, B. Silvi, *Comput. Chem.* **1999**, *23*, 597–604.
[35] J. V. Gauthier, T. R. Trautman, D. V. Jacobson, *Anal. Chim. Acta* **1991**, *246*, 211–225.
[36] B. D. Wladkowski, J. I. Brauman, *J. Am. Chem. Soc.* **1992**, *114*, 10643–10644.
[37] C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165–195. Note that the "resonance effects" for Me and $C_6H_5CH_2$, as measured by the σ_R^- parameter, are quite small (0.03 and 0.02, respectively).
[38] R. W. Taft, R. D. Topsom, *Prog. Phys. Org. Chem.* **1987**, *16*, 1–83.
[39] R. W. Taft, J.-L. M. Abboud, F. Anvia, M. Berthelot, M. Fujio, J.-F. Gal, A. D. Headley, W. G. Henderson, I. Koppel, J. H. Qian, M. Mishima, M. Taagepera, S. Ueji, *J. Am. Chem. Soc.* **1988**, *110*, 1797–1800.
[40] O. Mó, M. Yáñez, M. Eckert-Maksic, Z. B. Maksic, I. Alkorta, J. Elguero, *J. Phys. Chem. A* **2005**, *109*, 4359–4365.
[41] δ_RGA is linked to the ratio r of the ionization constants of RPH_2 and $RPH_2{\cdot}BH_3$ through the expression $\delta_R GA = -RT\ln r$. The values of δ_RGA given in Table 1 lead to r values ranging from 10^{13} to 10^{18}.
[42] a) G. A. Olah, R. Schlosberg, *J. Am. Chem. Soc.* **1968**, *90*, 2726–2727; b) G. A. Olah, *J. Am. Chem. Soc.* **1995**, *117*, 1393–1405; c) E. M. Arnett, J.-L. M. Abboud, *J. Am. Chem. Soc.* **1975**, *97*, 3865–3867.
[43] The equilibrium constant K_p is dimensionless and the various P involved in Equations (4) and (8) are divided by 1 bar.

Received: November 6, 2008