

# $\alpha$ -Stabilization by Silyl and Phosphino Substitution

Bettina Römer, Geo G. Gatev, Meili Zhong, and John I. Brauman\*

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305-5080

Received January 27, 1997

**Abstract:** The electron affinity of the bis(dimethylphosphino)methyl radical was measured to be  $35.3 \pm 0.2$  kcal/mol, using electron photodetachment spectroscopy in an ion cyclotron resonance spectrometer. Using equilibrium measurements,  $\Delta H_{\text{acid}}^{\circ}$  of bis(dimethylphosphino)methane and bis(trimethylsilyl)methane was determined to be  $370 \pm 3$  and  $373 \pm 3$  kcal/mol, respectively. From measured and known electron affinities and gas-phase acidities, we derive C–H bond dissociation energies: bis(dimethylphosphino)methane,  $92 \pm 3$  kcal/mol, and bis(trimethylsilyl)methane,  $95 \pm 3$  kcal/mol.  $\Delta H_{\text{acid}}^{\circ}$  of trimethylphosphine was bracketed at 383–387 kcal/mol. The  $\alpha$ -stabilization effect of silyl and phosphino substitution is large and comparable in size to stabilization by thio and chloro substitution. Possible mechanisms of stabilization are discussed.

## Introduction

The properties of a molecule, such as its acidity or equivalently the stability of its anion, can be changed dramatically by adding a substituent. Organic chemists have made use of the enhanced stability of silyl-substituted<sup>1,2</sup> and phosphino-substituted<sup>3</sup> anions in the synthesis of new carbon–carbon bonds, providing greater possibilities in such syntheses. Measuring the properties of substituted anions in the gas phase allows us to evaluate the stabilization provided by the substituents without solvation or counterion effects.

Substituent effects have been the subject of many gas-phase studies,<sup>4–11</sup> which have shown that  $\alpha$ -substitution with third-row elements stabilizes carbanions. From electron affinity and gas-phase acidity measurements, it is known that carbanions substituted with a silyl group are stabilized by about 20 kcal/mol<sup>6,12</sup> with respect to simple carbanions in which the electrons are typically weakly bound or unbound.<sup>13</sup> Gas-phase acidity measurements indicate similar stabilization for singly phosphino-substituted carbanions.<sup>5–7</sup> The electron affinity of doubly silyl-

substituted carbanions is increased by an additional 16 kcal/mol relative to the singly substituted compound.<sup>14</sup>

In this work, we examine further the effects of substitution on carbanions: we have determined the electron affinity of the bis(dimethylphosphino)methyl radical and the gas-phase acidities of trimethylphosphine, bis(dimethylphosphino)methane, and bis(trimethylsilyl)methane. Using known electron affinities and proton affinities,<sup>15</sup> we have also derived the corresponding bond dissociation energies. Comparing the thermochemical quantities for the different compounds, we evaluate the magnitude of stabilization for single and double  $\alpha$ -substitution.

Several factors can determine the stabilization upon substitution with third-row elements: the electronegativity of the substituent, its polarizability, the presence of d orbitals, hyperconjugation, and steric considerations.<sup>16–25</sup> By comparing the measured stabilization for single and double substitution with silyl and phosphino groups to known stabilization for thio and chloro groups, we can learn about the relative importance of the stabilizing and destabilizing factors. We contrast the effects of third-row substituents with those of second-row substituents.

## Experimental Section

**Photodetachment Experiments.** Photodetachment experiments were performed by using an ion cyclotron spectrometer (ICR) operating in the CW mode, which allows continuous generation and detection of

(1) Colvin, E. W. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier Science Ltd.: Oxford, 1995; Vol. 11, pp 131–354.

(2) Panek, J. S. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol 1, pp 579–627.

(3) Edwards, G. L. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Elsevier: Oxford, 1995; pp 105–171.

(4) Bartmess, J. E.; Hays, R. L.; Khatri, H. N.; Misra, R. N.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 4746–4751.

(5) Ingemann, S.; Nibbering, N. M. M. *J. Chem. Soc., Perkin Trans. 2* **1985**, 837–840.

(6) Damrauer, R.; Kass, S. R.; DePuy, C. H. *Organometallics* **1988**, *7*, 637–640.

(7) Grabowski, J. J.; Roy, P. D.; Leone, R. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1627–1632.

(8) Moran, S.; Ellison, G. B. *J. Phys. Chem.* **1988**, *92*, 1794–1803.

(9) Kass, S. R.; Guo, H.; Gahlke, G. D. *J. Am. Soc. Mass Spectrom.* **1990**, *1*, 366–371.

(10) Paulino, J. A.; Squires, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 5573–5580.

(11) Hierl, P. M.; Henchman, M. J.; Paulson, J. F. *Int. J. Mass Spectrom. Ion. Proc.* **1992**, *117*, 475–485.

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

(13) Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556–2558.

(14) Brinkman, E. A.; Berger, S.; Brauman, J. I. *J. Am. Chem. Soc.* **1994**, *116*, 8304–8310.

(15) Bartmess, J. E. *NIST Negative Ion Energetics Database, Version 3.0*; Standard Reference Database 19B, National Institute of Standard Technology, 1993.

(16) Bernardi, F.; Bottoni, A.; Tonachini, G. *Theor. Chim. Acta (Berlin)* **1979**, *52*, 37–43.

(17) Bernardi, F.; Mangini, A.; Tonachini, G.; Vivarelli, P. *J. Chem. Soc., Perkin Trans. 2* **1985**, 111–114.

(18) Bernardi, F.; Bottoni, A.; Venturini, A.; Mangini, A. *J. Am. Chem. Soc.* **1986**, *108*, 8171–8175.

(19) Bernardi, F.; Bottoni, A.; Valli, G. S.; Venturini, A. *Gazz. Chim. Ital.* **1990**, *120*, 301–307.

(20) Larson, J. R.; Epiotis, N. D. *J. Am. Chem. Soc.* **1981**, *103*, 410–416.

(21) Magnusson, E. *Aust. J. Chem.* **1985**, *38*, 23–46.

(22) Magnusson, E. *Tetrahedron* **1985**, *41*, 2945–2948.

(23) Rodriguez, C. F.; Sirois, S.; Hopkinson, A. C. *J. Org. Chem.* **1992**, *57*, 4869–4876.

(24) Schleyer, P. v. R.; et al. *J. Am. Chem. Soc.* **1984**, *106*, 6467–6475.

(25) Wiberg, K. B.; Castejon, H. *J. Am. Chem. Soc.* **1994**, *116*, 10489–10497.

ions.<sup>26</sup> The continuous mode provides a large signal-to-noise ratio, which allowed detection of small changes (less than 1%) in the ion population. A home-built capacitance bridge detector<sup>27</sup> allowed detection at a single frequency. A frequency lock<sup>27</sup> was employed to compensate for light-induced frequency shifts, ensuring that the signal was always measured at its maximum.

The low-resolution photodetachment spectrum was obtained by using a 1000-W Xe arc lamp (Canrad-Hanovia) with a 1/4 m grating monochromator (Kratos Analytical). The monochromator was calibrated by using a wavelength reversion spectroscopy (Beck) and the output of the calibrated laser system (see below). The bandwidth was about 20 nm. The power output of the arc lamp was recorded with use of a thermopile (Eppley Laboratory, Inc.) either immediately before or after the data collection.

The high-resolution spectrum was obtained by using a tunable dye laser (Coherent 590) pumped by an Ar-ion laser (Coherent Innova 200/15), using the laser dyes LDS821, LDS751, DCM, LDS698, and Rhodamine 6G (Exciton). Wavelengths were selected by using a three-plate birefringent filter (bandwidth 1 cm<sup>-1</sup>). The output of the dye laser was calibrated with a Ca/Ne optogalvanic lamp (Perkin-Elmer).<sup>28</sup> About 3% of the light was split off and directed into the thermopile, allowing power measurement during data collection.

Photodetachment spectra were recorded by monitoring decreases in the ion signal as a function of the energy (wavelength) of incident light. The data acquisition was controlled by an IBM XT. The signal was digitized by using an IBM Data Acquisition and Control Adapter Board.

At each new wavelength, a 4-s delay before data collection allowed for the reestablishment of an ion population at equilibrium. Typically, the signal was recorded for 2 s (15 000 readings) and the readings were averaged for every wavelength. Data were collected over a period of about 10 min to control baseline drift. The conditions of the experiments were adjusted so that the readings were less than 5 V, recorded to  $\pm 0.0025$  V. For low-resolution spectra, data were collected at intervals of 10 nm, while for high-resolution spectra, data were measured in 1-nm steps. A baseline reading of the ion signal without incident light was measured before and after the experiment.

Fractional decreases were calculated from the ion signal intensity with and without light (eq 1):

$$F(\lambda) = \frac{I_{\text{no light}} - I_{\text{light}}}{I_{\text{no light}}} \quad (1)$$

Cross sections were calculated from the fractional ion decreases and the intensity of the light by using the steady-state model (eq 2).<sup>29</sup>

$$\sigma(\lambda) = \frac{F(\lambda)}{\text{power} \times \lambda \times [1 - F(\lambda)]} \quad (2)$$

A minimum of three scans were averaged for every wavelength region. These regions were chosen to overlap with one another so that they could be spliced together to produce the photodetachment spectrum.

**Equilibrium and Acidity-Bracketing Experiments.** Equilibrium and acidity-bracketing experiments were carried out in an Ionspec OMEGA Fourier-transform mass spectrometer with use of impulse excitation.<sup>30</sup> Mass-selective ion ejection was achieved by using standard double resonance techniques.

In equilibrium and acidity-bracketing measurements, the extent of proton transfer between the species of interest and a reference acid is monitored by measuring the relative abundances of the ions. Equilibrium experiments follow the proton-transfer reaction between HA, the species of interest, and the conjugate base B<sup>-</sup> of a reference acid HB (eq 3).

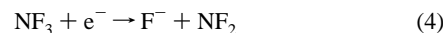


If after sufficient time both ions can still be detected but the ion concentrations do not change, we assume that the proton-transfer reaction has reached equilibrium. To confirm that an equilibrium is established, we first ejected one ion and waited until a constant ratio of ion concentrations was observed. We then ejected the other ion and again monitored the concentrations. If the same final ratio is achieved starting from both directions, the equilibrium constant can be measured for that proton-transfer reaction, assuming the pressures are known. The pressures of the neutrals were monitored with an ion gauge (Granville Phillips, Model 330) that was calibrated against a capacitance manometer (MKS Baratron Type 170-39A). These equilibrium constant measurements were performed at varying pressures and on different days. The results were reproducible to  $\pm 10\%$ .

Acidity-bracketing measurements were used to bound the acidity of the desired compound if an equilibrium could not be established. The acidity of the species of interest, HA, is determined by observing whether the proton-transfer reaction between HA and the conjugate base of a reference acid, HB, occurs or whether the reverse reaction occurs. If eq 3 proceeds in the forward direction, the reference acid HA is more acidic than HB; if the reverse reaction occurs, HB is more acidic than HA. The acidity of HA can be bracketed by using reference acids of greater and of lesser acidity than that of HA.

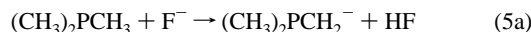
**Materials.** Nitrogen trifluoride (Ozark-Mahoning) was used as the neutral precursor for fluoride anion. Bis(trimethylsilyl)methane and trimethylphosphine were obtained from Aldrich, and bis(dimethylphosphino)methane was obtained from Strem Chemicals. Because of the pyrophoric nature of the phosphines, the samples were handled in a vacuum line or under nitrogen in a glovebag. The reference acids, tetramethylsilane, acetonitrile, methanol, and propene, were also commercially available (Aldrich). All compounds were freeze-pump-thawed several times before being admitted to the ICR cell.

**Ion Generation.** The primary ion, fluoride, was generated via dissociative capture of low-energy electrons (<1 eV) by nitrogen trifluoride, eq 4.

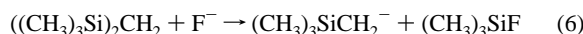


In some cases, hydroxide ion was used as the primary ion. It was formed via dissociative electron capture ( $\sim 6$  eV) by water.

The desired secondary ions were prepared by proton abstraction from the corresponding neutrals, eq 5.



(Trimethylsilyl)methyl anion was generated from bis(trimethylsilyl)methane by nucleophilic displacement of a trimethylsilyl group by fluoride, eq 6.



**Calculations.** AM1 and HF/6-31G\* calculations were performed by using the Spartan Molecular Modeling Package,<sup>31</sup> fully optimizing molecular geometries. Neutral and anion studies used the restricted Hartree-Fock (RHF) model, and calculations on the radicals used the unrestricted Hartree-Fock (UHF) model.

## Results

**Photodetachment.** The electron photodetachment spectrum of bis(dimethylphosphino)methyl anion is shown in Figure 1. At low resolution, the photodetachment cross section rises from zero at 726 nm. In the high-resolution spectrum (Figure 1), the cross section rises above zero at  $809 \pm 5$  nm and continues

(26) Lehman, T. A.; Bursley, M. M. *Ion Cyclotron Resonance Spectrometry*; Wiley-Interscience: New York, 1976.

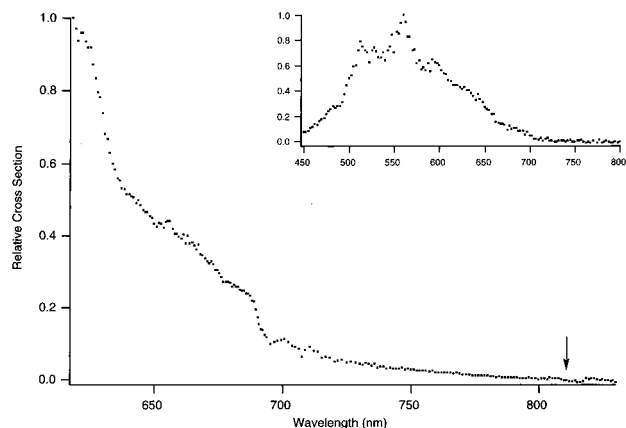
(27) Marks, J.; et al. *Rev. Sci. Instrum.* **1987**, *58*, 1460-1463.

(28) M.I.T. *Wavelength Tables—Wavelengths by Element*; M.I.T. Press: Cambridge, 1982; Vol. 2.

(29) Zimmerman, A. H. Ph.D. Thesis, Stanford University, 1977.

(30) Zhong, M.; Brauman, J. I. *J. Am. Chem. Soc.* **1996**, *118*, 636-641.

(31) *Wave function Spartan Molecular Modelling Package*; Wave function Inc.: Irvine, CA, 1995.

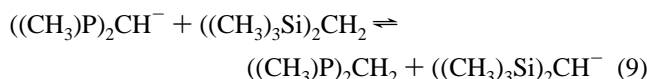
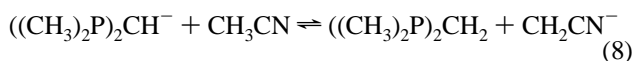
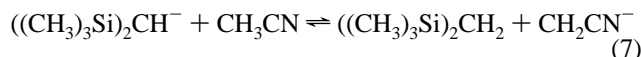


**Figure 1.** High-resolution photodetachment spectrum of the bis-(dimethylphosphino)methyl anion, with the low-resolution spectrum shown in the insert. The arrow indicates the assignment of the electron affinity.

to increase smoothly. Because the signal-to-noise ratio is much larger in the high-resolution spectra, we can observe small amounts of photodetachment which might not be visible in the low-resolution experiments. We assign the electron affinity to be  $35.3 \pm 0.2$  kcal/mol ( $1.53 \pm 0.01$  eV).

The low-resolution photodetachment spectrum of the bis-(dimethylphosphino)methyl anion displays a maximum in the cross section at higher energies. We attribute this to a transition to an excited electronic state of the anion embedded in the neutral plus electron continuum.<sup>32</sup> The observed peak lies between approximately 610 and 500 nm, placing this excited state  $2.2 \pm 0.3$  eV above the ground state of the anion. Similar excitations have been observed previously in mono-silyl-substituted anions<sup>12</sup> and bis-silyl-substituted anions.<sup>14</sup>

**Equilibrium Measurements.** The gas-phase acidities of bis-(trimethylsilyl)methane and bis(dimethylphosphino)methane were determined by equilibrium measurements with acetonitrile ( $\Delta H_{\text{acid}}^{\circ}(\text{CH}_3\text{CN}) = 372.9 \pm 2.6$  kcal/mol;<sup>33</sup> eqs 7 and 8) and confirmed by measuring the equilibrium between the two compounds of interest (eq 9).



The equilibrium constants for eqs 7, 8, and 9 were determined to be  $2.97 \pm 0.07$ ,  $0.025 \pm 0.002$ , and  $0.010 \pm 0.001$ , respectively. Within experimental error, the equilibrium constant measured for reaction 9 equals the ratio of the equilibrium constant of reaction 8 to that of reaction 7, showing that our measurements are internally consistent. By using the measured equilibrium constants and the estimated reaction temperature of 350 K,<sup>34</sup>  $\Delta G^{\circ}$  for the reactions are  $-0.7 \pm 0.03$ ,  $+2.6 \pm 0.1$ , and  $+3.2 \pm 0.07$  kcal/mol, respectively.

To determine  $\Delta H_{\text{acid}}^{\circ}$ , we need to evaluate the entropy

(32) Zimmerman, A. H.; Gygas, R.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 5595–5597.

(33) Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6047–6056.

**Table 1.** Acidity Bracketing Reactions of  $(\text{CH}_3)_3\text{P}^a$

AH	$\Delta G_{\text{acid}}^{\circ}$	$\Delta H_{\text{acid}}^{\circ}$	proton transfer?	
			$\text{A}^- + (\text{CH}_3)_3\text{P}$	$(\text{CH}_3)_2\text{PCH}_2^- + \text{AH}$
$\text{H}_2\text{O}$	$384.1 \pm 0.5^b$	$390.8 \pm 0.2^b$	YES	NO
$(\text{CH}_3)_4\text{Si}$	$381.6 \pm 2.0^c$	$390.9 \pm 2.1^c$	YES <sup>d</sup>	NO
MeOH	$374.0 \pm 1.9^b$	$380.5 \pm 2.15^b$	NO	YES

<sup>a</sup> All values in kcal/mol. <sup>b</sup> Reference 15. <sup>c</sup> Reference 12. <sup>d</sup> Slow reaction.

change,  $\Delta S^{\circ}$ . Cumming and Kebarle<sup>35</sup> and Bartmess, Scott, and McIver<sup>33,36</sup> have shown that the change in entropy for deprotonation depends primarily on changes in internal rotations and symmetry. Electronic, vibrational, and translational entropy terms are usually similar for the acid and the corresponding anion and cancel out. For eq 9, any changes in symmetry and rotations should approximately cancel each other, given the similar structure of the respective acids and anions. Thus  $\Delta S^{\circ}$  should be approximately zero.

For reactions 7 and 8, we observe that acetonitrile loses an internal rotation upon deprotonation, suggesting a lower entropy. For the silyl- and phosphino-substituted compounds, however, calculations have shown that, upon deprotonation, the C–X (X = P, Si) bond distance decreases by  $0.1 \text{ \AA}$ <sup>14,17,23,24</sup> and a large barrier to rotation exists.<sup>25</sup> This indicates that the C–X bond has double bond character upon deprotonation and that these molecules also lose an internal rotation. We therefore expect that the change in  $\Delta S^{\circ}$  due to changes in internal rotations can be neglected.  $\Delta S^{\circ}$  should depend only on the symmetry change in the reactions, and we thus take  $T\Delta S^{\circ}$  to be  $<0.3$  kcal/mol.<sup>35</sup> We determine  $\Delta H_{\text{acid}}^{\circ}$  for bis(trimethylsilyl)methane and bis-(dimethylphosphino)methane to be  $373 \pm 3$  and  $370 \pm 3$  kcal/mol, respectively.

**Acidity-Bracketing Measurements.** We were not able to observe an equilibrium reaction for trimethylphosphine, because few reference acids with suitable acidities are available, and we could not adjust the concentration of the reference acids to achieve equilibrium. In addition, it was difficult to get a stable signal of the conjugate base of trimethylphosphine, primarily because we could not achieve stable pressures of the neutral. We therefore bracketed its proton affinity using several reference acids (Table 1).

Trimethylphosphine reacted with hydroxide and reacted slowly with the trimethylsilylmethyl anion, but it did not react with methoxide (detection limit  $\leq 1\%$ ). (Dimethylphosphino)-methyl anion showed no reaction with water or tetramethylsilane (detection limit  $\leq 1\%$ ), but did react with methanol.<sup>37</sup> We believe that we would have detected an anion concentration of

(34) Han, C.-C.; Brauman, J. I. *J. Am. Chem. Soc.* **1989**, *111*, 6491–6496.

(35) Cumming, J. B.; Kebarle, P. *Can. J. Chem.* **1978**, *56*, 1–9.

(36) Bartmess, J. E.; McIver, R. T., Jr. In *Gas-Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, pp 87–121.

(37) Our acidity measurement of (dimethylphosphino)methane agrees with the measurement previously done by Grabowski.<sup>7</sup> Consistent with Grabowski's report, we also did not observe the equilibrium reaction between water and (dimethylphosphino)methane reported earlier by Ingemann and Nibbering.<sup>5</sup>

(38) Seakins, P. W.; Pilling, M. J.; Niiranene, J. T.; Gutman, D.; Krasnoperov, L. N. *J. Phys. Chem.* **1992**, *96*, 9847–9855.

(39) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744–2765.

(40) Damrauer, Kass, and DePuy<sup>6</sup> have reported a proton affinity for the trimethylsilylmethyl anion of 387.3 kcal/mol based on bracketing reactions. The standards used in that work were not known to high accuracy, however, so we have chosen to use the value from the thermochemical cycle.

**Table 2.** Electron Affinities, Gas-Phase Acidities, and Bond Dissociation Energies of Silyl- and Phosphino-Substituted Methanes, R-H<sup>a</sup>

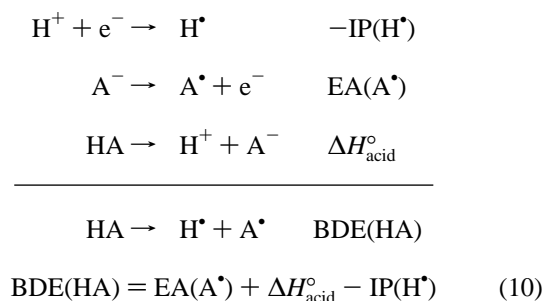
R	EA(R <sup>•</sup> )	$\Delta H_{\text{acid}}^{\circ}(\text{RH})$	BDE(RH)
CH <sub>3</sub>	1.8 ± 0.7 <sup>b</sup>	416.6 ± 1.0 <sup>c</sup>	104.9 ± 1.0 <sup>d</sup>
(CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub>	21.9 ± 0.3 <sup>e</sup>	390.9 ± 2 <sup>e</sup> 387.3 ± 3 <sup>f</sup>	99.2 ± 1.2 <sup>g</sup>
(CH <sub>3</sub> ) <sub>2</sub> PCH <sub>2</sub>	26 <sup>c</sup>	384 ± 3 <sup>h,i</sup>	96 <sup>j</sup>
((CH <sub>3</sub> ) <sub>3</sub> Si) <sub>2</sub> CH	36.0 ± 0.2 <sup>k</sup>	373 ± 3 <sup>i</sup>	95 ± 3 <sup>c</sup>
((CH <sub>3</sub> ) <sub>2</sub> P) <sub>2</sub> CH	35.3 ± 0.2 <sup>i</sup>	370 ± 3 <sup>i</sup>	92 ± 3 <sup>c</sup>

<sup>a</sup> All values in kcal/mol. <sup>b</sup> Reference 13. <sup>c</sup> Calculated by using the thermochemical cycle (eq 10). <sup>d</sup> References 38 and 39. <sup>e</sup> Reference 12. <sup>f</sup> References 6 and 40. <sup>g</sup> Reference 41. <sup>h</sup> Reference 7. <sup>i</sup> This work. <sup>j</sup> Estimated from similar compounds, see text. <sup>k</sup> Reference 14.

1% in an equilibrium reaction. Given the neutral concentrations, this corresponds to an equilibrium constant of 0.013, so that the difference in acidity between the reference acid and trimethylphosphine must be at least 3.0 kcal/mol. From this, we determined the  $\Delta H_{\text{acid}}^{\circ}$  range of trimethylphosphine to be 383 to 387 kcal/mol, supporting Grabowski's measurement of 384 ± 3 kcal/mol.<sup>7</sup>

## Discussion

With our results, we can determine the bond dissociation energies for the silyl and phosphino compounds using the thermochemical cycle (eq 10).



By comparing the electron affinities, proton affinities, and bond dissociation energies for the different compounds, we can evaluate the magnitude of single and double  $\alpha$ -stabilization by third-row elements. Aided by calculations, we attempt to understand the effects of silyl and phosphino substitution on the structure and energetics of molecular carbanions.

**Stabilization by Third-Row Elements.** The electron affinity measures the stability of an anion relative to its corresponding neutral (eq 11).



By comparing electron affinities, we can learn about the relative stabilization of the anions compared to the radicals. The electron affinities are summarized in Table 2.

The electron affinity of the methyl radical is 1.8 kcal/mol.<sup>13</sup> Upon substitution with one dimethylphosphino group, the electron affinity increases to 26 kcal/mol (based on an estimate of the bond dissociation energy, see below). Substitution by a second dimethylphosphino group increases the electron affinity further to 35.3 kcal/mol. These effects are very large and similar in magnitude to the effects of silyl substitution, where the electron affinity increases to 21.9 kcal/mol for one silyl group,<sup>12</sup> and further to 36.0 kcal/mol for bis-silyl substitution.<sup>14</sup> Thus, the magnitude of stabilization due to substitution in  $\alpha$ -phos-

phino-substituted carbanions is very large and similar to that in silyl systems. Single substitution increases the electron affinity by about 20–24 kcal/mol; the addition of a second substituent further increases the electron affinity by 9–14 kcal/mol.

We have determined several gas-phase acidities,  $\Delta H_{\text{acid}}^{\circ}$ , which correspond to the relative stabilities of the anions to the respective protonated neutrals (eq 12). If we assume that the substituents primarily influence these reactions by their effect on the anions,<sup>42</sup> we can learn about the relative stabilities of the anions by comparing acidities. A summary of acidities is shown in Table 2.



$\Delta H_{\text{acid}}^{\circ}$  of methane has been determined to be 416.6 kcal/mol by using the thermochemical cycle and known electron affinity and bond dissociation energy.<sup>13,38,39</sup> Single substitution on the methyl carbon by a trimethylsilyl group increases the acidity to 390.9 kcal/mol, and substitution by a dimethylphosphino group increases the acidity to 384 kcal/mol. Double substitution on the methyl carbon by silyl increases the acidity to 373 kcal/mol for bis(dimethylsilyl)methane, in excellent agreement with the previous estimate<sup>14</sup> of 374 kcal/mol, which was based on a measured electron affinity and an estimated bond strength. Double phosphino substitution increases the acidity further to 370 kcal/mol for bis(dimethylphosphino)methane. The bond dissociation energies in these compounds are similar (see below). Consequently, we expect the acidities to mirror the electron affinities, which is indeed the case.

Bond dissociation energies (eq 13) can be measured directly or can be derived with the thermochemical cycle by using electron affinities and acidities (eq 10). A summary of the known and derived bond dissociation energies for silyl- and phosphino-substituted methanes is given in Table 2.



The C–H bond dissociation energy in methane is 104.9 kcal/mol.<sup>38,39</sup> Single substitution on the methyl carbon by a trimethylsilyl group decreases the BDE to 99.2 kcal/mol,<sup>41</sup> about the same as substitution by a methyl group. We estimate the bond dissociation energy of (dimethylphosphino)methane because the electron affinity of its conjugate base is not known. Comparing the values listed in Table 2, we observe that silyl and phosphino substitution have similar effects on acidities and electron affinities. Also, we observe a decrease in BDE's upon single substitution with a silyl group and little change upon second substitution. We expect the BDE for (dimethylphosphino)methane to follow the same trends and estimate it to be 96 kcal/mol, yielding an electron affinity of 26 kcal/mol. Adding a second substituent gives a C–H BDE of 95 kcal/mol for bis(trimethylsilyl)methane and of 92 kcal/mol for bis-(dimethylphosphino)methane.

We now compare the effects of  $\alpha$ -substitution by silyl and phosphino groups to those due to  $\alpha$ -substitution by other third-row elements. Chloro substitution has been studied experimentally,<sup>15,43–45</sup> while not much is known about the effects of

(42) If the stabilities of the neutrals can be accounted for by using simple additivity relationships (such as Benson additivities), then we can attribute the substituent effect on acidity to changes in anion stabilization.

(43) Ingemann, S.; Nibbering, N. M. M. *Can J. Chem.* **1984**, *62*, 2273–2281.

(44) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532.

(45) Bohme, D. K.; Lee-Ruff, E.; Young, L. B. *J. Am. Chem. Soc.* **1972**, *94*, 5153–5159.

(41) Doncaster, A. M.; Walsh, R. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 2908–2916.

**Table 3.** Electron Affinities, Gas-phase Acidities, and Bond Dissociation Energies of Thio- and Chloro-Substituted Methanes, R-H<sup>a</sup>

R	EA(R <sup>•</sup> )	$\Delta H_{\text{acid}}^{\circ}(\text{RH})$	BDE(RH)
CH <sub>3</sub>	1.8 ± 0.7 <sup>b</sup>	416.6 ± 1.0 <sup>c</sup>	104.9 ± 1.0 <sup>d</sup>
CH <sub>3</sub> SCH <sub>2</sub>	20.0 ± 1.2 <sup>e</sup>	393.2 ± 2.1 <sup>c</sup>	99.6 ± 2.4 <sup>b</sup>
ClCH <sub>2</sub>	18.9 ± 5.5 <sup>c</sup>	395.6 ± 3.6 <sup>f</sup>	100.9 ± 3.2 <sup>g</sup>
Cl <sub>2</sub> CH	38.5 ± 3.9 <sup>c</sup>	374.1 ± 3.8 <sup>h</sup>	99.0 ± 1.0 <sup>g</sup>
Cl <sub>3</sub> C	52.6 ± 6.3 <sup>c</sup>	356.7 ± 6.2 <sup>h</sup>	95.7 ± 1.0 <sup>g</sup>

<sup>a</sup> All values in kcal/mol. <sup>b</sup> Reference 13. <sup>c</sup> Calculated by using the thermochemical cycle (eq 10). <sup>d</sup> References 38 and 39. <sup>e</sup> Reference 8. <sup>f</sup> Reference 5. <sup>g</sup> Reference 44. <sup>h</sup> Reference 15.

thio substitution. The known electron affinities, proton affinities, and bond dissociation energies of thio- and chloro-substituted methanes are summarized in Table 3.

For the thio and chloro compounds as well, the electron affinity changes dramatically upon substitution. Single substitution by a thio or chloro group on the methyl radical increases the electron affinity by 17–18 kcal/mol. Further substitution increases the electron affinity by 20 kcal/mol for a second chlorine, and an additional 14 kcal/mol for a third chlorine. Interestingly, the second chlorine substituent shows less saturation than is observed in the silyl and phosphino compounds.

The bond energies in this series are also similar, relatively independent of the substituent, so the acidities show the same behavior as the electron affinities.

Considering the different electronegativities of these third-row substituents, it is interesting that the observed stabilization is so similar across the row. The electronegativity of a substituent is often important in the stabilization of an anion.<sup>46</sup> In addition, factors such as polarization, lone pair–lone pair electron repulsion, hyperconjugative interactions, and inclusion of d orbitals must contribute to the overall stability. A combination of these factors should explain the observed trends, although it is difficult to quantify the impact of each one. The effects are often interconnected in some fashion and are dependent on the specific substituent,<sup>47</sup> but we can make some qualitative evaluation of the impact of the different factors for the different substituents.

Electronegativity, polarizability, hyperconjugation, and inclusion of d orbitals have a stabilizing effect on anions by withdrawing or distributing charge, while lone pair–lone pair repulsions are destabilizing. The presence of each factor manifests itself by changing the geometry or charge distribution in the substituted compound compared to the unsubstituted one. An electron-withdrawing substituent localizes negative charge near itself and away from the carbanion center. A polarizable substituent affects the electron density by redistributing the electron density over a larger part of the molecule, again away from the carbanion. Hyperconjugation also changes the electron distribution, but its most noticeable effect is the bond shortening of the C–X bond due to increased orbital interactions. Lone pair–lone pair repulsion results in bond lengthening. d-Orbital participation can affect the geometry of the molecule.<sup>18,23,24</sup> By calculating geometries, charge distribution, and bond orders, it is possible to predict the importance of these stabilizing and destabilizing factors.

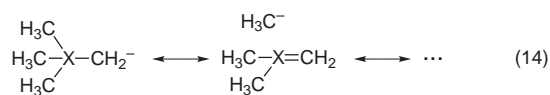
(46) March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1992; pp 175–181.

(47) Bernardi and co-workers have tried to separate effects in several studies by varying basis sets and geometry optimization parameters in their calculations.<sup>16–19</sup>

(48) Brauman, J. I.; Blair, L. K. *J. Am. Chem. Soc.* **1970**, *92*, 5986–5992.

(49) Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6056–6063.

For silyl and phosphino substitution, calculations<sup>14,17,23,24</sup> have shown that the C–X bond decreases significantly (by about 0.1 Å) upon deprotonation and the central H–C–X bond angle increases. Our calculations for phosphino substitution reproduce these results. Wiberg and Castejon have recently studied the origin of the increased stability of the carbanion of dimethyl sulfide relative to that of the carbanion of dimethyl ether.<sup>25</sup> They calculate a decrease in C–X bond length,<sup>25</sup> indicating that thio substitution facilitates significant negative hyperconjugation, eq 14, stabilizing the carbanion, while methoxy substitution does not facilitate such stabilization. Important additional evidence for hyperconjugation is the calculated increase in barrier height for rotation, as well as variation of bond length during rotation.<sup>25</sup> We find the same effect for the phosphino-substituted carbanions. The inclusion of d-orbitals has been shown to have negligible effects when comparing the stability of an anion relative to the respective neutral because it stabilizes both the anion and the neutral to an equal extent.<sup>18,24,25</sup>



Lone pair–lone pair repulsions reduce the overall stabilization of anions, while polarization effects enhance it.<sup>18,20,24,48,49</sup> In contrast to substitution with a silyl, phosphino, or thio group, chloro substitution results in a lengthening of the X–CH<sub>2</sub> bond. The chloro-substituted compound cannot be stabilized by hyperconjugation. The observed substituent effect can be attributed to the large electronegativity of chlorine. The relative importance of the stabilizing factors undoubtedly plays an important role in determining the effectiveness as substituents are added.

In summary,  $\alpha$ -substitution by third-row elements causes large stabilization of the anion relative to the radical and the protonated neutral. Upon further substitution, the stabilization increases. The relative importance of the contributing effects depends on the substituent. It is clear that only a combination of factors can explain the observed trends. While it is difficult to quantify the impact of each of the different factors, we believe that hyperconjugation is most important for silyl and phosphino substitution and that electronegativity is most important for chloro substitution. Thio substitution is probably more equally affected by both of those. Taking into consideration the varying importance of stabilizing and destabilizing factors, it is interesting how similar the magnitudes of stabilization are to each other.

**Stabilization by Second-Row Elements.** We can compare the stabilization effect of substitution by third-row elements to the effect of substitution by second-row elements. The data are incomplete, because some thermochemical parameters for second-row substituents have not yet been determined, but a few trends can still be noted. The known electron affinities, gas-phase acidities, and bond dissociation energies for methanes substituted by second row elements are summarized in Table 4.

Electron affinities are not known for all of the multiply substituted compounds, but some trends can be seen. Single substitution by (CH<sub>3</sub>)<sub>3</sub>C increases the electron affinity slightly, while substitution by CH<sub>3</sub>O lowers it slightly. Most strikingly, double substitution by fluorine has a large stabilizing effect of 26 kcal/mol, and triple substitution provides an additional stabilization of 14 kcal/mol.

The acidities of methanes substituted with a *tert*-butyl, amino, methoxy, or fluoro group increase by about 8–10 kcal/mol relative to methane itself. Additional fluoro substitution greatly

**Table 4.** Electron Affinities, Gas-Phase Acidities, and Bond Dissociation Energies of Methanes, R–H, Substituted by Second-Row Elements<sup>a</sup>

R	EA(R <sup>•</sup> )	$\Delta H_{\text{acid}}^{\circ}(\text{RH})$	BDE(RH)
CH <sub>3</sub>	1.8 ± 0.7 <sup>b</sup>	416.6 ± 1.0 <sup>c</sup>	104.9 ± 1.0 <sup>d</sup>
(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub>	4.8 ± 1 <sup>e</sup>	408.9 ± 2 <sup>e</sup>	101.1 ± 1 <sup>d</sup>
(CH <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub>		>404 <sup>g</sup>	99.7 ± 1 <sup>f</sup>
CH <sub>3</sub> OCH <sub>2</sub>	0 ± 2 <sup>c</sup>	407 ± 2.0 <sup>i</sup>	84 ± 2 <sup>h</sup>
FCH <sub>2</sub>	4.6 ± 4 <sup>c</sup>	409 ± 4.0 <sup>j</sup>	93.0 ± 1 <sup>h</sup>
F <sub>2</sub> CH	27.9 ± 3.7 <sup>c</sup>	389 ± 3.5 <sup>j</sup>	100 ± 2 <sup>h</sup>
F <sub>3</sub> C	42.4 ± 2.7 <sup>c</sup>	377.0 ± 2.1 <sup>l</sup>	103 ± 1.0 <sup>k</sup>
			105.8 ± 1.7 <sup>m</sup>

<sup>a</sup> All values in kcal/mol. <sup>b</sup> Reference 13. <sup>c</sup> Calculated by using the thermochemical cycle (eq 10). <sup>d</sup> References 38 and 39. <sup>e</sup> Reference 50. <sup>f</sup> Reference 41. <sup>g</sup> Reference 5. <sup>h</sup> Reference 44. <sup>i</sup> Reference 51. <sup>j</sup> Reference 52. <sup>k</sup> Reference 53. <sup>l</sup> Reference 49. <sup>m</sup> Reference 15.

stabilizes methane upon double and triple substitution: A second substituent stabilizes the singly fluoro-substituted compound by an additional 20 kcal/mol for a total stabilization of 27 kcal/mol. Trifluoromethane is further stabilized by 12 kcal/mol, giving a total stabilization of 39 kcal/mol compared to methane itself. Calculated acidities by Hopkinson et al.<sup>23</sup> have suggested that fluorine substituents have a synergistic effect.

Bond dissociation energies for C(CH<sub>3</sub>)<sub>3</sub>, N(CH<sub>3</sub>)<sub>2</sub>, OCH<sub>3</sub>, and F substituents are lowered by varying amounts (4, 20, 12, and 4 kcal/mol, respectively). Multiple substitution by fluorine raises the bond dissociation energy—for double substitution, the bond dissociation energy is almost identical to that of the unsubstituted methane, for triple substitution it is increased even further.

In general, third-row elements stabilize carbanions more effectively than the corresponding second-row elements. Many theoretical papers have addressed this issue.<sup>17–19,22–25,54</sup> The consensus is that several factors are favorable for the stabilization by third-row elements relative to that of their corresponding second-row elements: the increased electropositive and polariz-

able nature<sup>19,20,23</sup> and the greater orbital overlap for negative hyperconjugation.<sup>25,54</sup> The third-row elements are electropositive, so the X–CH<sub>3</sub> bonds are polarized with the greater part of the electron density on the CH<sub>3</sub> group. Thus, the coefficient in the bonding orbital is large for the CH<sub>3</sub> group and small for the X atom. Conversely, in the antibonding orbital, the coefficient is small for the CH<sub>3</sub> group and large for the X atom.<sup>12</sup> The electronegativity of the second-row substituents is larger than that of their third-row counterparts, but this effect appears to play a relatively minor role in the difference in stabilization between the two rows.

## Summary

From acidity-bracketing and equilibrium measurements, we have measured the acidities for trimethylphosphine, bis(dimethylphosphino)methane, and bis(dimethylsilyl)methane. We have measured the electron photodetachment spectrum of the bis(dimethylphosphino)methyl anion, from which we have extracted the electron affinity of the corresponding radical. Using the measured thermochemical quantities, we determined the bond dissociation energies of the corresponding neutrals. We have evaluated the magnitude of  $\alpha$ -stabilization by silyl and phosphino substituents.

**Acknowledgment.** We are grateful to the National Science Foundation for support of this research.

JA970279S

(50) DePuy, C. H.; Bierbaum, V. M.; Damrauer, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 1968–1973.

(51) DePuy, C. H.; Bierbaum, V. M.; Damrauer, R. *J. Am. Chem. Soc.* **1984**, *106*, 4051–4053.

(52) Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2517–2529.

(53) Pickard, J. M.; Rodgers, A. S. *Int. J. Chem. Kinet.* **1983**, *15*, 569–577.

(54) Salzner, U.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1993**, *115*, 10231–10236.