# JOC Article

Theoretical and Experimental Investigation of the Basicity of Phosphino(silyl)carbenes

David Martin,[†,‡] Ona Illa,[§] Antoine Baceiredo,*[,†] Guy Bertrand,[†,‡] Rosa M. Ortuño,*[,§] and Vicenç Branchadell*[,§]

Laboratoire d'Hétérochimie Fondamentale et Appliquée, UMR CNRS 5069, Université Paul Sabatier, 118, route de Narbonne, F-31062 Toulouse Cedex 04, France, UCR-CNRS Joint Research Chemistry Laboratory, UMR 2282, Department of Chemistry, University of California, Riverside, California 92521-0403, and Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain

baceired@chimie.ups-tlse.fr; rosa.ortuno@uab.es; vicenc@klingon.uab.es

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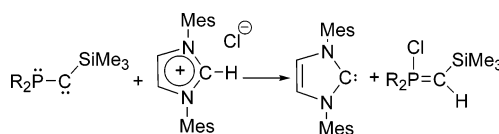
The reactivity of phosphino(trimethylsilyl)carbenes **1** with several organic acids has been examined in order to evaluate the pK_a values of the conjugate acids. Carbenes **1** react efficiently with *C*-organic acids such as 1,3-dimesitylimidazolium chloride, phenylacetylene, acetonitrile, and acetyltrimethylsilane, which have pK_a's in DMSO in the range 18−31. However, the reaction of the conjugate acids **1**H$^+$ with the anion perturbs the determination of the genuine basicity of **1**. Theoretical calculations have been performed in order to quantify the basicity of phosphino(trimethylsilyl)-carbenes **1** and to compare them with that of N-heterocyclic carbenes **2**. The pK_a of **1**H$^+$ in DMSO has been computed to be in the 23.0−23.4 range, so that **1** is not strong enough as a base to spontaneously deprotonate organic acids such as phenylacetylene, acetonitrile, or acetyltrimethylsilane. However, its conjugate acid **1**H$^+$ is a strong electrophile and easily reacts with the nucleophilic conjugate bases of these acids leading to the formation of the corresponding phosphorus ylides.

Introduction

Since the discoveries of the first two families of stable singlet carbenes, the phosphino(silyl)carbenes **1**[1] and the imidazol-2-ylidenes **2**,[2] numerous studies have been carried out on their reactivity and electronic structure,[3] with both types of carbene clearly being strongly nucleophilic. The acid−base chemistry of **2** and related N-heterocyclic carbenes (NHCs) has been the subject of recent work.[4] The pK_a of the conjugate acids **2**H$^+$ was estimated to be between 16.6 and 24.4 in DMSO, depending on the nature of the R substituent.[4c] These values are in agreement with the experimental results concern-

ing the protonation reactions of **2** with organic acids. Indeed, the 1,3-dimesitylimidazol-2-ylidene **2b** was protonated by a phenol (pK_a = 18, in DMSO), while only a hydrogen bond interaction was observed with diphenylamine (pK_a = 25, in DMSO) (Chart 1).[5]

(3) For recent reviews, see: (a) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (b) Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1276. (c) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2001**, *46*, 181. (d) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951. (e) Alder, R. W.; Blake, M. E.; Chaker, M. E.; Harvey, J. N.; Paolini, F.; Schutz, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 5896. (f) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239−2246. (g) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247−2273. (h) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Chem. Soc. Rev.* **2004**, *33*, 619−636. (i) Enders, D.; Balensiefer, T. *Acc. Chem. Res.* **2004**, *37*, 534. (j) Kirmse, W. *Angew. Chem., Int. Ed.* **2004**, *43*, 1767. (k) Bertrand, G. In *Reactive Intermediates Chemistry*; Moss, R. A., Platz, M. S., Jones, M., Jr., Eds.; Wiley: New York, 2004; pp 329−374. (l) Canac, Y.; Soleilhavoup, M.; Conejero, S.; Bertrand, G. *J. Organomet. Chem.* **2004**, *689*, 3857.

(4) (a) Alder, R. W.; Allen, P. R.; Williams, S. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1267. (b) Alder, R. W.; Blake, M. E.; Oliva, J. M. *J. Phys. Chem. A* **1999**, *103*, 11200. (c) Kim, Y.-J.; Streitwieser, A. *J. Am. Chem. Soc.* **2002**, *124*, 5757. (d) Lee, M.-T.; Hu, C.-H. *Organometallics* **2004**, *23*, 976. (e) Magill, A. M.; Cavell, K. J.; Yates, B. F. *J. Am. Chem. Soc.* **2004**, *126*, 8717.
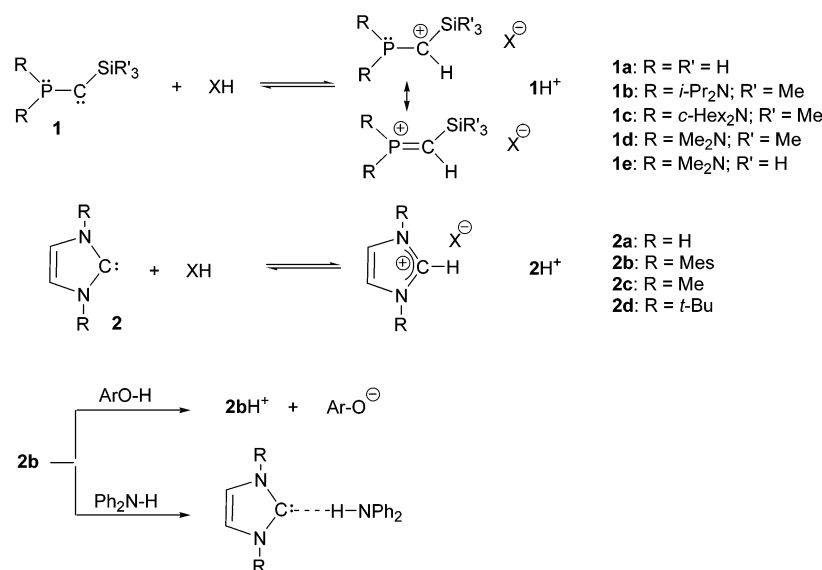
† Université Paul Sabatier.
‡ University of California.
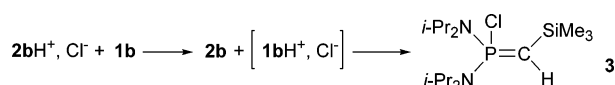§ Universitat Autònoma de Barcelona.

(1) (a) Igau, A.; Grützmacher, H.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1988**, *110*, 6463. (b) Igau, A.; Baceiredo, A.; Trinquier, G.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 621. (c) Bourissou, D.; Bertrand, G. *Adv. Organomet. Chem.* **1999**, *44*, 175.

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

CHART 1

1a: R = R' = H
1b: R = *i*-Pr₂N; R' = Me
1c: R = *c*-Hex₂N; R' = Me
1d: R = Me₂N; R' = Me
1e: R = Me₂N; R' = H

2a: R = H
2b: R = Mes
2c: R = Me
2d: R = *t*-Bu

SCHEME 1

Here, we report on the reactions between the stable phosphino(silyl)carbenes **1b,c** and several *C*-organic acids. Theoretical calculations were performed to support and rationalize the experimental results.

Results and Discussion

The proton affinities for each of the parent carbenes **1a** and **2a** have already been calculated[6] and are very similar, 257.0 and 257.3 kcal/mol, respectively, which suggests that the corresponding conjugate acids **1H⁺** and **2H⁺** have somewhat similar pK_a values. Therefore, we first studied the reaction of phosphino(silyl)carbene **1b** with imidazolium chloride **2bH⁺, Cl⁻**, in order to compare their basicity. A clean reaction took place, and the NHC **2b** was obtained quantitatively along with the P-chlorophosphorus ylide **3** (Scheme 1). Indeed, methylenephosphonium ions such as **1bH⁺** are highly electrophilic species[7] and quickly react with the anion to give the corresponding phosphorus ylide **3**. At a first glance, this observation indicates that phosphino(silyl)carbene **1b** is more basic than NHC **2b** and should deprotonate organic acids with pK_a values lower than 24 in DMSO.

Although phosphino(silyl)carbenes **1b,c** react with electron-poor olefins to give the corresponding cyclopropanes with a total *syn* diastereoselectivity,[8] no reactions were observed with internal alkynes. In contrast, addi-

SCHEME 2
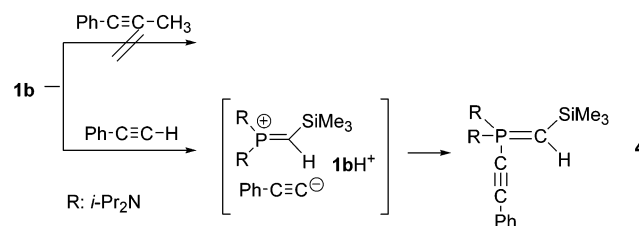
SCHEME 3
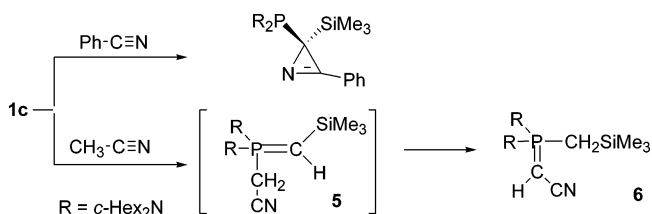
tion at room temperature of carbene **1b** to phenylacetylene cleanly leads to phosphorus ylide **4**, which was isolated in 85% yield. It seems reasonable to postulate that there is initial formation of the acetylide, which quickly reacts with the methylenephosphonium **1bH⁺** (Scheme 2)

It is known that phosphino(silyl)carbenes **1b,c** cleanly undergo [2 + 1] cycloaddition reactions with benzonitrile giving rise to the corresponding 2-phosphino-2*H*-azirines.[9] In marked contrast, carbene **1c** readily reacts with acetonitrile to give phosphorus ylide **6** (Scheme 3). The P=CH−CN sequence was confirmed by the ¹³C NMR ¹H-coupled signal of the cyano group, which appears as

(5) Cowan, J. A.; Clyburne, J. A. C.; Davidson, M. G.; Harris, R. L. W.; Howard, J. A. K.; Küpper, P.; Leech, M. A.; Richards, S. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 1432.

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

(7) (a) Igau, A.; Baceiredo, A.; Grützmacher, H.; Pritzkow, H.; Bertrand, G. *J. Am. Chem. Soc.* **1989**, *111*, 6853. (b) Grützmacher, H.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 709. (c) Guerret, O.; Bertrand, G. *Acc. Chem. Res.* **1997**, *30*, 486. (d) Frenking, G.; Fau, S.; Marchand, C. M.; Grützmacher, H. *J. Am. Chem. Soc.* **1997**, *119*, 6648. (e) Grützmacher, H.; Marchand, C. M. *Coord. Chem. Rev.* **1997**, *163*, 287

(8) (a) Goumri-Magnet, S.; Kato, T.; Gornitzka, H.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **2000**, *122*, 4464. (b) Krysiak, J.; Kato, T.; Gornitzka, H.; Baceiredo, A.; Mikolajczyk, M.; Bertrand, G. *J. Org. Chem.* **2001**, *66*, 8240. (c) Krysiak, J.; Lyon, C.; Baceiredo, A.; Gornitzka, H.; Mikolajczyk, Bertrand, G. *Chem. Eur. J.* **2004**, *10*, 1982.

(9) (a) Alcaraz, G.; Wecker, U.; Baceiredo, A.; Dahan, F.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1246. (b) Piquet, V.; Baceiredo, A.; Gornitzka, H.; Dahan, F.; Bertrand, G. *Chem. Eur. J.* **1997**, *3*, 1757. (c) Piquet, V.; Baceiredo, A.; Dahan, F.; Bertrand, G. *C. R. Acad. Sci. Ser. IIc* **1998**, 123. (d) Déborah, A.; Mazières, S.; Piquet-Fauré, V.; Gornitzka, H.; Baceiredo, A.; Bertrand, G. *Chem. Eur. J.* **2002**, *8*, 5306.

SCHEME 4
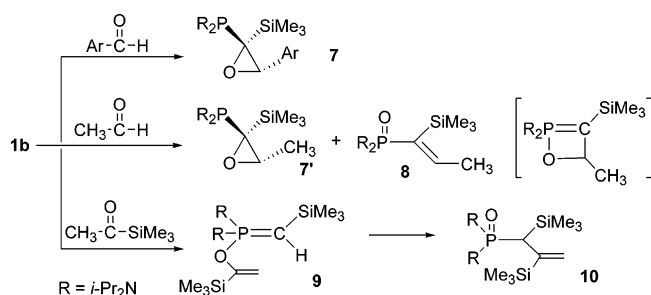
a doublet of doublets ($^2J_{PC}$ = 8 Hz and $^2J_{CH}$ = 4 Hz). Not surprisingly, the initially formed phosphorus ylide **5** was not observed due to a rapid 1,3-proton shift leading to the more stable isomer **6**.

We have already shown that phosphino(silyl)carbene **1b** reacts with aromatic[10] aldehydes through a [2 +1] cycloaddition, affording the corresponding oxiranes **7** with excellent diastereoselectivity. When aliphatic aldehydes such as acetaldehyde were used, in addition to the formation of oxirane **7′**, a small amount of olefin **8** was observed; the latter results from a [2 + 2]-like cyclo-addition giving an oxaphosphetene intermediate which undergoes ring opening.[11] To prevent both of these processes, carbene **1b** was reacted with the enolizable, sterically hindered (methyl)(trimethylsilyl)ketone. Here, a very clean reaction was observed and olefin **10** was isolated in near-quantitative yield (Scheme 4). Most probably, the initially formed enolate reacts with the transient methylenephosphonium ion **1bH⁺** to give the phosphorus ylide **9**, which undergoes a rearrangement to afford the observed product **10**. Indeed, ylide **9** can be detected by monitoring the reaction using multinuclear NMR spectroscopy. The ^{31}P NMR chemical shift (+54 ppm) is in the range expected for such ylides, with the ylidic carbon appearing as a doublet (10.8 ppm, $^1J_{C,P}$ = 162 Hz) in the ^{13}C NMR spectrum. The driving force for the rearrangement of **9** into **10** is the formation of a phosphine oxide fragment.

Since clean acid−base reactions occurred between carbenes **1b,c** and organic acids with pK_a's in the range 18−25, we turned our attention to the mechanism of the reaction between **1b,c** and DMSO.[1a] Indeed, two alterna-tive pathways for the formation of sulfur ylide **13** can be considered: (i) a [2 + 2] cycloaddition reaction with the formation of a transient four-membered ring or (ii) an acid−base reaction involving the deprotonation of DMSO by carbene **1** followed by the *O*-alkylation of **1H⁺** to give **11**. Then, **11** could rearrange into **12** (as observed for **9** → **10**), and finally a prototropic rearrangement may occur leading to the observed product **13**, which is obviously
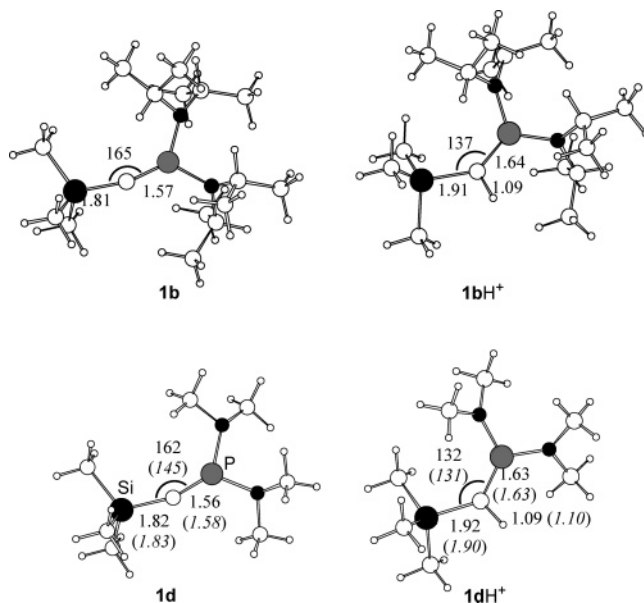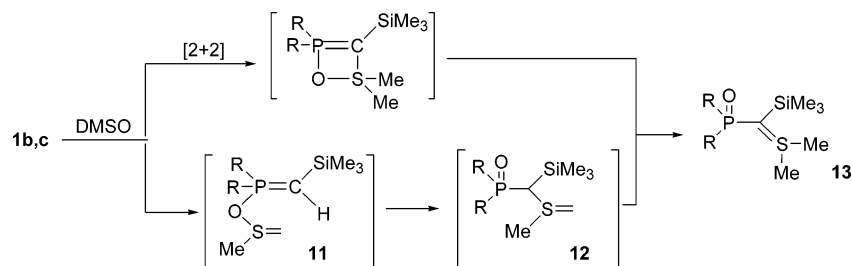
FIGURE 1. Structures of carbenes **1b** and **1d** and their conjugate acids obtained at the B3LYP/6-31+G(d,p) level of calculation. Bond lengths in Å and bond angles in deg. Values obtained in DMSO solution are shown in parentheses.

thermodynamically more stable than **12** because of the presence of two electron-withdrawing groups at the ylidic carbon (Scheme 5).

This acid−base pathway would imply that the pK_a values of **1b,c**H⁺ would be greater than that of DMSO (35 in DMSO). However, the situation is obviously not so simple since the conjugate acids **1H⁺** are highly electrophilic and readily react with the anion to give a more stable phosphorus ylide. Certainly, the latter reac-tion perturbs the experimental determination of the true basicity of phosphino(silyl)carbenes **1**.

To gain a better understanding of the reactivity of carbenes **1** with *C*-organic acids theoretical calculations were performed for reactions involving carbenes **1b** (R = *i*-Pr₂N) and **1d** (R = Me₂N).

Theoretical Calculations. Figure 1 presents the optimized structures of **1b**, **1d**, and their respective conjugate acids. The most stable conformation of the isopropyl groups in **1b** has been determined through a preliminary exploration of the potential energy surface at the B3LYP/3-21G level of calculation.

The structures of **1b** and **1d** can be compared with the crystal structure of a related phosphino(silyl)carbene which bears Me₂Si(*t*BuN)₂P as phosphino group (C−Si = 1.795 Å, P−C = 1.53 Å, and Si−C−P= 152°).[12] The largest differences are observed for the C−P bond and

SCHEME 5

TABLE 1. Gas-Phase Deprotonation Enthalpies[a] of Several Acids XH Obtained at Different Levels of Calculation

XH	B3LYP[b]	PBE1PBE[b]	CBS-QB3	expt
pyrazole	354.7 (355.2)	355.9 (356.4)		353.7[13]
TMS-CO-Me	360.8 (360.1)			
PhCCH	368.9 (370.2)	369.7 (370.8)		370.6[14]
MeCN	372.0 (371.7)	372.7 (372.6)		372.9,[14] 373.3[15]
DMSO	376.9 (376.5)	377.5 (377.1)		373.5,[14] 374.3[15]
2aH$^+$	252.6 (252.7)		251.7	
2cH$^+$	261.1 (261.3)	261.4 (261.8)	258.3[4e]	
2dH$^+$	270.4 (270.1)		266.8[4e]	
1aH$^+$	238.6 (236.7)		235.4	
1bH$^+$	273.9 (274.4)			
1dH$^+$	267.2 (268.2)			
1eH$^+$	263.0 (263.5)		261.3	

^{a} In kcal mol^{-1} at 1 atm and 298.15 K. ^{b} For geometries optimized with the 6-31+G(d,p) basis set. Values computed with the 6-311+G(2d,2p) basis set are shown in parentheses.

for the Si−C−P bond angle. Protonation produces a remarkable variation in the Si−C−P bond angle, along with a lengthening of the C−Si and C−P bonds. When the geometries were optimized in DMSO solution, the major change was observed for the Si−C−P bond angle in **1d**, which is more acute (145°).

Table 1 shows the values of the gas-phase deprotonation enthalpies computed for the conjugated acids of several phosphino(silyl)carbenes **1**, diaminocarbenes **2** and for organic acids involved in reactions with **1** (see Schemes 2−5). We have also included pyrazole, since it has been used by Yates et al.[4e] as a reference for computing relative pK_a's in DMSO.

The comparison between computed and experimental values shows that B3LYP leads to better results than PBE1PBE. In particular, the mean relative errors are 1.7 and 1.8 kcal mol^{-1}, respectively, while the maximum deviations are obtained in both cases for DMSO (3.0 and 3.6 kcal mol^{-1}, respectively). The use of the 6-311+G-(2d,2p) basis set improves the results and reduces the mean relative error and maximum deviation to 1.5 and 2.6 kcal mol^{-1}, respectively.

The gas-phase deprotonation enthalpies of **2c**H$^+$ (R = Me) and **2d**H$^+$ (R = *t*-Bu) were recently computed at the CBS-QB3 level of calculation, which is expected to provide very accurate thermochemical results.[4e] The values computed for these two systems at the B3LYP/6-311+G(2d,2p)//B3LYP/6-31+G(d) level of calculation overestimate the enthalpies by 3.0−3.3 kcal mol^{-1}. The use of the CBS-QB3 method for phosphino(silyl)carbenes such as **1b** and **1d** is not possible with our computational resources due to the size of the systems and the lack of symmetry. To get an estimate of the error introduced in the B3LYP calculation of deprotonation enthalpies, we studied two simple models, **1a** (R = R′ = H) and **1e** (R = NMe$_2$, R′ = H). We also considered the model diaminocarbene **2a** (R = H). The comparison between B3LYP and CBS-QB3 shows that, in all cases, B3LYP overesti-

mates the deprotonation enthalpies. The differences between B3LYP and CBS-QB3 are 1.0 kcal mol^{-1} for **2a**, 1.3 kcal mol^{-1} for **1a**, and 2.2 kcal mol^{-1} for **1e**. In view of these results and those obtained for **2c** and **2d**, we estimate that the CBS-QB3 deprotonation enthalpies of **1b**H$^+$ and **1c**H$^+$ would be 2−3 kcal mol^{-1} lower than the B3LYP values. According to these results, **1b** is more basic in the gas phase than any of the diamino carbenes studied.[4e]

In the next step, the pK_a's of acids involved in reactions with **1** were computed in DMSO. The absolute pK_a of XH can be computed from the standard Gibbs reaction energy associated with the reaction

$$XH \rightarrow X^- + H^+$$
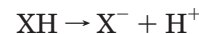
in DMSO solution ($\Delta G°_{DMSO}$) through

$$pK_a = \Delta G°_{DMSO}/2.303RT$$

This Gibbs reaction energy is computed from

$$\Delta G°_{DMSO} = \Delta G°_{gas} + \Delta\Delta G_{solv} + \Delta G_{corr}$$

where $\Delta G°_{gas}$ is the Gibbs reaction energy in the gas phase, $\Delta\Delta G_{solv}$ is the contribution from solvation and is calculated from

$$\Delta\Delta G_{solv} = \Delta G_{solv}(X^-) + \Delta G_{solv}(H^+) - \Delta G_{solv}(XH)$$

and ΔG_{corr} is the correction associated to the change in standard state from gas phase (1 atm) to solution (1 mol L^{-1}) and its value at 298.15 K is 1.89 kcal mol^{-1}.[14]

The value we used for the Gibbs solvation energy of the proton in DMSO is −268.6 kcal mol^{-1},[16] derived from the experimental value in water (−264.0 kcal mol^{-1})[17] and the Gibbs energy of proton transfer from water to DMSO (−4.6 kcal mol^{-1}).[18] This value slightly differs from the one used by Yates et al.,[4e] which was chosen to minimize the absolute difference between the calculated absolute and relative pK_a's.

Three different approaches for treating the solvent effects were used: (a) the CPCM method using gas-phase geometries (CPCM//gas), (b) the IPCM method using gas-phase geometries (IPCM//gas), and (c) the CPCM method using geometries optimized in solution (CPCM//CPCM). The results are summarized in Table 2.

If we compare the values obtained using gas-phase geometries, we observe that the CPCM method provides values in closer agreement with experiment than the IPCM method. The optimization of geometries in solution does not generally lead to an improvement of results.

For **2d**H$^+$, **1b**H$^+$, and **1d**H$^+$ we also computed relative pK_a's from

$$pK_a(XH) = pK_a(RH) - \Delta G°_{DMSO}/2.303RT$$

(10) Illa, O.; Gornitzka, H.; Baceiredo, A.; Bertrand, G.; Branchadell, V.; Ortuño, R. M. *J. Org. Chem.* **2003**, *68*, 7707.

(11) Illa, O.; Gornitzka, H.; Branchadell, V.; Baceiredo, A.; Bertrand, G.; Ortuño, R. M. *Eur. J. Org. Chem.* **2003**, 3147.

(12) Kato, T.; Gornitzka, H.; Baceiredo, A.; Savin, A.; Bertrand, G. *J. Am. Chem. Soc.* **2000**, *122*, 998.

(13) Taft, R. W.; Anvia, F.; Taagepera, M.; Catalan, J.; Elguero, J. *J. Am. Chem. Soc.* **1986**, *108*, 3237.

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

(15) Cummings, J. B.; Kebarle, P. *Can. J. Chem.* **1978**, *56*, 1.

(16) Chipman, D. M. *J. Phys. Chem. A* **2002**, *106*, 7413.

(17) Tissandier, M. D.; Cowen, K. A.; Feng, W. Y.; Gundlach, E.; Cohen. M. H.; Earhart, A. D.; Coe, J. V.; Tuttle, T. R., Jr. *J. Phys. Chem. A* **1998**, *102*, 7787.

TABLE 2. pK_a's of Acids XH

XH	CPCM//gas	IPCM//gas	CPCM//CPCM	expt[20]
pyrazole	20.2	17.5	20.2	19.8
TMS-CO-Me	24.1	21.1	26.0	24.4[21]
PhCCH	27.3	24.7	27.9	28.8
MeCN	29.8	30.4	30.5	31.3
DMSO	36.8	37.1	37.3	35.1
2dH$^+$	23.1 (22.8)^a	23.6		22.7[4c]
1bH$^+$	23.4 (23.0)^a			
1dH$^+$	22.8 (22.4)^a			

^{a} Values relative to pyrazole are shown in parentheses.

where the reference acid RH is pyrazole and $\Delta G°_{DMSO}$ is the standard Gibbs reaction energy associated to the proton-transfer reaction

$$RH + X^- \rightarrow R^- + XH$$
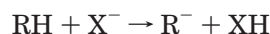
in DMSO solution. The results obtained have been included in Table 2.

The pK_a's of phenylacetylene, acetonitrile, and DMSO can be compared with the values reported by Almerindo *et al.*[23] (29.0, 34.6, and 38.1, respectively). Our results for acetonitrile and DMSO are closer to experiment, whereas for phenylacetylene Almerindo's result is better than ours. The pK_a of phenylacetylene has also been computed by Fu *et al.*[24] (27.1). Finally, the values obtained for **2d**H$^+$ can be compared with those reported by Yates *et al.*[4e] for absolute (22.6) and relative (22.8) pK_a's.

From our results we estimate that the pK_a of **1b**H$^+$ is in the 23–23.4 range, slightly above the value corresponding to **2d**H$^+$, so that **1b** is also more basic than **2d** in DMSO solution.

Since we have seen that phosphino(silyl)carbene **1b** is able to react with several *C*-organic acids (Schemes 2–5), we studied the reactions between **1d** and these organic acids XH in the gas phase and in toluene solution.

These reactions can be conceptually broken down into two steps:

$$(1)\ XH + \textbf{1d} \rightarrow X^- + \textbf{1d}H^+$$

$$(2)\ X^- + \textbf{1d}H^+ \rightarrow X\text{-}\textbf{1d}H$$
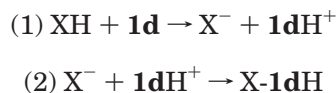
In this way, the roles played by the basicity of **1b** and the electrophilicity of its conjugate acid can separated. The gas-phase reaction enthalpies and Gibbs reaction energies associated with these two steps are shown in Table 3.

(18) Marcus, Y.; Kamlet, M. J.; Taft, R. W. *J. Phys. Chem.* **1988**, *92*, 3613.

(19) (a) Liptak, M. D.; Shields, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 7314. (b) Saracino, G. A. A.; Improta, R.; Barone, V. *Chem. Phys. Lett.* **2003**, *373*, 411.

(20) (a) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456. (b) Bordwell pK_a Table: http://www.chem.wisc.edu/areas/reich/pkatable/kacont.htm.

(21) The pK_a in DMSO was estimated from its value in water (16.42)[17] and the linear fitting obtained from the values of pK_a's in DMSO and water of acetone, acetonitrile, phenylacetylene, dimethyl sulfoxide and pyrrole:[15] pK_a(DMSO) = 13.3 + 0.6763pK_a(water) (n = 5, r = 0.990).

(22) Kresgue, A. J.; Tobin, J. B. *J. Am. Chem. Soc.* **1990**, *112*, 2805.

(23) Almerindo, G. I.; Tondo, D. W.; Pliego, J. R., Jr. *J. Phys. Chem. A* **2004**, *108*, 166.

(24) Fu, Y.; Rui-Qiong, L.; Guo, Q.-X. *J. Am. Chem. Soc.* **2004**, *126*, 814.

TABLE 3. Reaction Enthalpies and Gibbs Reaction Energies^a Computed for the Reactions between 1d and Several Organic Acids in the Gas Phase

XH	$\Delta H°_1$	$\Delta H°_2$	$\Delta H°_1 + \Delta H°_2$	$\Delta G°_1$	$\Delta G°_2$	$\Delta G°_1 + \Delta G°_2$
TMS-CO-Me	93.6	−125.0	−31.4	93.6	−109.8	−16.2
PhCCH	101.8	−139.8	−38.0	102.3	−127.6	−25.3
MeCN	104.8	−135.0	−30.2	105.4	−121.7	−16.3
DMSO	109.8	−139.3	−29.5	111.1	−126.9	−15.8

^{a} Computed at the B3LYP/6-31+G(d,p) level of calculation. In kcal mol^{-1} at 1 atm and 298.15 K.
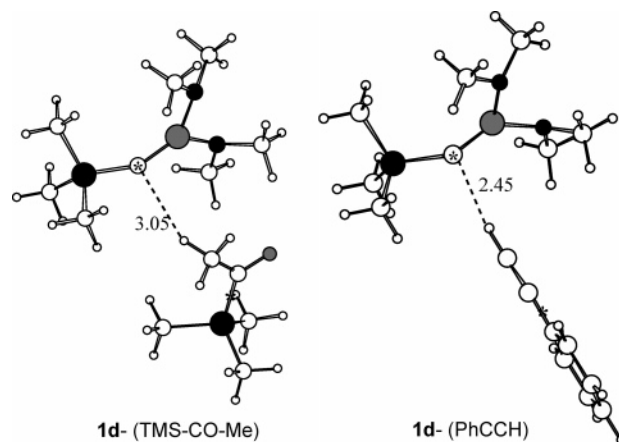

FIGURE 2. Structures of **1d**–XH complexes obtained at the B3LYP/6-31G+G(d,p) level of calculation. Interatomic distances in Å. Asterisks indicate the points that were used for estimating the distance between ions in hypothetical ion pairs.

In the gas phase, the proton transfer from XH to **1d** is very endothermic. The values of the reaction enthalpy range between 93.6 and 109.8 kcal mol^{-1}. For **1b** these values would decrease by 6.8 kcal mol^{-1}.

According to Alkorta et al.,[25] if $\Delta H°_1$ is lower than 102 kcal mol^{-1} spontaneous proton transfer could be produced in the gas phase since the energy cost for proton transfer may be compensated by the stabilizing interaction between both ions in the ion pair. In Table 3 there are two cases, TMS-CO-Me and PhCCH, which satisfy this condition. For these two systems we tried to locate the corresponding ion pairs, but in all attempts the system evolved either to the X-**1d**H products or to the XH-**1d** complexes. The structures of these complexes are shown in Figure 2, and the corresponding formation enthalpies are 2.1 and 0.2 kcal mol^{-1}, respectively.

The structures of these complexes can be used to estimate the formation energy of hypothetical ion pairs in the gas phase. If we take as an estimate of the distance between the **1d**H$^+$ and X$^-$ ions in the ion pairs as being the distances from the carbene carbon atom to the midpoint of the Si−C(carbonyl) bond of TMS-CO-Me (5.1 Å), and to the midpoint of the C−C(ring) bond of phenylacetylene (5.5 Å) in the intermediates shown in Figure 2, the stabilization energies obtained from the Coulomb interaction energies are −65.1 and −60.4 kcal mol^{-1}, respectively. These interaction energies are not sufficient to make the proton transfer favorable in the gas phase. To compensate for the energy cost associated

(25) Alkorta, I.; Rozas, I.; Mó, O.; Yáñez, M.; Elguero, J. *J. Phys. Chem. A* **2001**, *105*, 7481.

TABLE 4. Gibbs Reaction Energies[a] Computed for the Reactions between 1d and Several Organic Acids in Toluene Solution

XH	ΔG°_1	ΔG°_2	$\Delta G^\circ_1 + \Delta G^\circ_2$
TMS-CO-Me	40.9	−59.6	−18.7
PhCCH	46.6	−73.3	−26.7
MeCN	52.8	−71.2	−18.4
DMSO	58.6	−74.5	−15.9

[a] Computed at the B3LYP/6-31+G(d,p) level of calculation. In kcal mol^{-1} at 1 mol L^{-1} and 298.15 K

to proton transfer, the distances between ions in hypothetical ion pairs should be 3.7 Å (TMS-CO-Me) and 3.3 Å (phenylacetylene). The size of molecules prevents the distance between the **1d**H$^+$ and X$^-$ ions from becoming short enough to overcome the energy necessary to form the ions.

Table 4 presents the results obtained for the reactions in toluene solution using the gas phase optimized geometries and the CPCM method for solvation. The Gibbs reaction energies associated with the proton transfer notably decrease with respect to the values in the gas phase (see Table 3), but the process is still thermodynamically unfavorable. Regarding the second step, the corresponding Gibbs energies become less negative. As a result, the Gibbs reaction energies for the overall reactions do not significantly change with respect to the gas phase (see Table 3).

For TMS-CO-Me and phenylacetylene the estimated stabilization energies of ion pairs in toluene ($\epsilon = 2.379$) are −27.4 and −25.4 kcal mol^{-1}, respectively. In addition to this stabilization, the formation of an ion pair also involves an entropic destabilization. Assuming that the entropy variation is the same as the one involved in the formation of the hydrogen bond complexes shown in Figure 2 (−31 and −29 cal mol^{-1} K^{-1}, respectively), our estimates for the Gibbs energy of stabilization for the ion pairs are −18.1 kcal mol^{-1} for TMS-CO-Me and −16.7 kcal mol^{-1} for phenylacetylene. From these results, we estimate that the proton transfer from XH to **1d** to form a **1d**H$^+$,X$^-$ ion pair involves a Gibbs reaction energy of about 23 kcal mol^{-1} for TMS-CO-Me and 30 kcal mol^{-1} for phenylacetylene.

To provide a better insight on the reactions of **1d** with acids XH, we located the transition states corresponding to the overall reactions. These transition states are shown in Figures 3 and 4, and the corresponding Gibbs activation energies are presented in Table 5. Transition states were obtained in the gas phase except for the reaction with MeCN, where the location was only possible in toluene solution.

For the reaction with phenylacetylene the computed Gibbs activation energy in toluene solution (26.1 kcal mol^{-1}) is notably lower than the 46.6 kcal mol^{-1} computed for the formation of the separated ions (see Table 4) and close to our estimate for the formation of the ion pair (30 kcal mol^{-1}). Indeed, this transition state (**TS-4d**) can be considered as an ion pair, where the proton has already been transferred from phenylacetylene to **1d**, while the formation of the new P−C bond has not yet begun. The normal coordinate associated to the imaginary frequency corresponds to a displacement of the PhCC moiety between H and P atoms of the protonated carbene moiety.
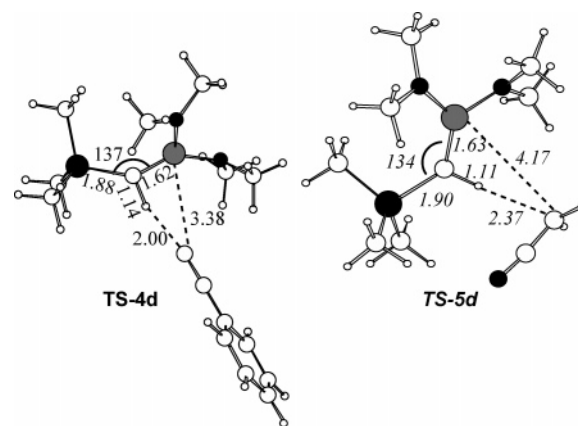
FIGURE 3. Transition states corresponding to the reactions of **1d** with phenylacetylene (**TS-4d**) and acetonitrile (**TS-5d**) obtained at the B3LYP/6-31G+G(d,p) level of calculation. Interatomic distances in Å and bond angles in deg. The structure and values obtained in toluene solution are shown in italics.
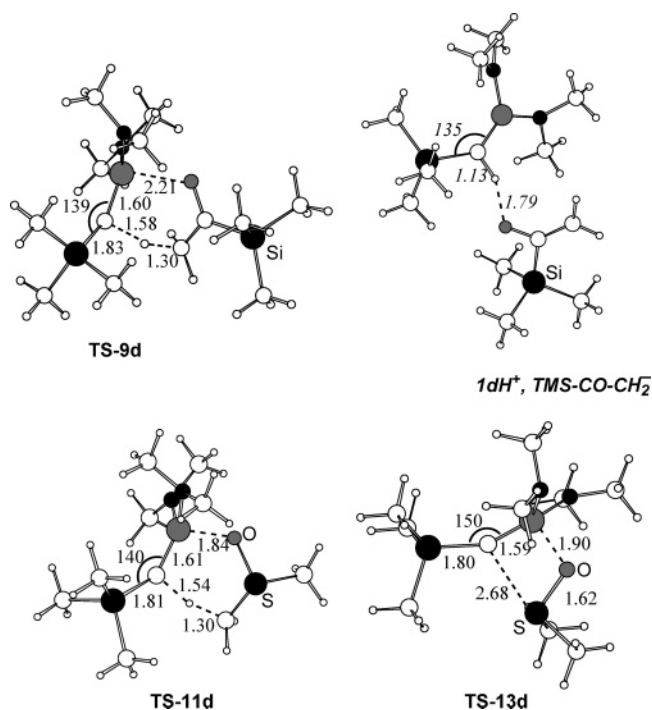
FIGURE 4. Transition state corresponding to the reaction of **1d** with acetyltrimethylsilane (**TS-9d**), **1d**H$^+$ TMS-CO-CH$_2^-$ ion pair, and transition states corresponding to the reactions of **1d** with dimethyl sulfoxide (**TS-11d** and **TS-13d**) obained at the B3LYP/6-31+G(d,p) level of calculation. Interatomic distances in Å and bond angles in deg. The structure and values obtained in toluene solution are shown in italics.

A geometry optimization starting from the transition state confirmed that it leads to the formation of **4d**.

The transition state corresponding to the reaction with acetonitrile (**TS-5d**) also resembles an ion pair. The Gibbs activation energy is larger than the value corresponding to phenylacetylene, in good agreement with their relative acidities.

The transition state obtained for the reaction of **1d** with and TMS-CO-Me (**TS-9d** in Figure 4) does not correspond to an ion pair and the proton transfer takes

TABLE 5. Gibbs Activation Energies[a] for the Reactions between 1d and Organic Acids XH

XH	TS[b]	gas phase	toluene[c]
TMS-CO-Me	**TS-9d**	30.8	28.9
PhCCH	**TS-4d**	34.9	26.1
MeCN	**TS-5d**		33.6
DMSO	**TS-11d**	30.7	30.7
	TS-13d	22.1	22.8

[a] Computed at the B3LYP/6-31+G(d,p) level of calculation. In kcal mol^{-1} at 298.15 K and 1 atm (gas phase) or 1 mol L^{-1} (toluene). [b] See Figures 3 and 4. [c] Gas-phase geometries except for MeCN.

place simultaneously with formation of the P—O bond. The value of the Gibbs activation energy in toluene solution (28.9 kcal mol^{-1}) is larger than our estimate for the formation of the **1d**H$^+$, X$^-$ ion pair (23 kcal mol^{-1}) so that it is likely that the reaction takes place through the ion pair in solution. We have been able to optimize the geometry for such an ion pair in toluene solution and the corresponding structure has been included in Figure 4. The Gibbs formation energy for this ion pair is 20.8 kcal mol^{-1}, a value very close to our previous estimate. This ion pair is about 30.5 kcal mol^{-1} above the reaction product in terms of Gibbs energy; however, the presence of a CH····OC hydrogen bond prevents it from collapsing to the reaction product.

For the reaction between **1d** and DMSO we have located two different transition states corresponding to the two paths shown in Scheme 5. Table 5 indicates that the most favorable path is the [2 + 2]-like cycloaddition through **TS-13d**. This transition state directly leads to the formation of **13d**, so that the four-membered ring shown in Scheme 5 is not a minimum of the potential energy surface. The alternative pathway involving the deprotonation of DMSO by **1d** through **TS-11d** is kinetically less favorable. In this case, the formation of a **1d**H$^+$,X$^-$ ion pair is not expected to be favored, since DMSO is a very weak acid. Thus, the reactivity of DMSO with phosphino(silyl)carbenes is not related to acid—base reactions.

Conclusions

According to the experimental results, the phosphino-(silyl)carbenes **1b,c** behave as strong bases in the presence of several *C*-organic acids with pK_a's in the 24–31 range. From theoretical calculations, we can estimate that phosphino(silyl)carbene **1b** is more basic than diamino carbene **2d** both in the gas phase and in DMSO. In particular, the estimated pK_a of **1b**H$^+$ is in the 23–23.4 range. The theoretical study of the reactions in toluene solution, shows that **1** is not strong enough as a base to spontaneously deprotonate the organic acids with which it reacts. However, the conjugate acid **1**H$^+$ is a strong electrophile which reacts further to form a covalent adduct with whatever counterion is present.

Experimental Section

Reaction of Carbene 1b with 2bH$^+$. A THF-d_8 solution (400 μL) of carbene **1b** (147 mg, 0.47 mmol) was added at −30 °C to a THF-d_8 solution (100 μL) of 1 equiv of **2b**H$^+$, Cl$^-$. After the solution was warmed to room temperature, multinuclear NMR spectroscopy indicated the quantitative formation of ylide **3**[26] and NHC **2b**.[27]

Reaction of Carbene 1b with Phenylacetylene. One equivalent of phenylacetylene (65 mg, 0.6 mmol) was added at room temperature to a toluene solution (3 mL) of carbene **1b** (200 mg, 0.6 mmol). After the solvent was removed under vacuum, ylide **4** was extracted with pentane and obtained as a yellow oil (210 mg, 85%): ^{31}P NMR (C$_6$D$_6$) δ 18; ^{1}H NMR (C$_6$D$_6$) δ 0.50 (s, 9 H), 1.30 (d, $^3J_{HH}$ = 7 Hz, 12 H), 1.36 (d, $^3J_{HH}$ = 7 Hz, 12 H), 3.79 (d sept, $^3J_{PH}$ = 16 Hz, $^3J_{HH}$ = 7 Hz, 4 H), 6.95 (m, 3 H), 7.46 (m, 2 H); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 4.4 (d, $^3J_{PC}$ = 4 Hz), 14.5 (d, $^1J_{PC}$ = 145 Hz), 23.5 (s), 24.3 (s), 46.7 (d, $^2J_{PC}$ = 4 Hz), 90.0 (d, $^1J_{PC}$ = 172 Hz), 99.2 (d, $^2J_{PC}$ = 31 Hz), 129.3 (s), 129.7 (s), 131.9 (s), 132.7 (s).

Reaction of Carbene 1c with Acetonitrile. Acetonitrile (70 μL, 1.3 mmol) was added at room temperature to a toluene solution (3 mL) of carbene **1c** (200 mg, 0.4 mmol). The resulting mixture was stirred at room temperature for 4 h, and the progress of the reaction was monitored by ^{31}P NMR spectroscopy. The ylide **6** was extracted with pentane and obtained as a colorless oil (130 mg, 58%): ^{31}P NMR (CDCl$_3$) δ 62.3; ^{1}H NMR (CDCl$_3$) δ 0.21 (s, 9 H), 1.18 (d, $^2J_{PH}$ = 12 Hz, 1 H), 1.34 (d, $^2J_{PH}$ = 19 Hz, 2 H), 1.70 (m, 40 H), 3.29 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ 0.9 (d, $^3J_{CP}$ = 3 Hz), 11.4 (d, $^1J_{CP}$ = 168 Hz), 20.1 (d, $^1J_{CP}$ = 83 Hz), 25.7–35.2 (m), 56.5 (d, $^2J_{CP}$ = 5 Hz), 130.1 (d, $^2J_{CP}$ = 8.0 Hz); IR (toluene) 2148 cm^{-1}; MS (CI, NH$_3$) 518 (M + H). Anal. Calcd for C$_{30}$H$_{56}$N$_3$SiP: C, 69.58; H, 10.90; N, 8.11. Found: C, 70.12; H, 11.22; N, 8.38.

Reaction of Carbene 1b with Acetyltrimethylsilane. One equivalent (47 μL, 0.3 mmol) of acetyltrimethylsilane was added at room temperature to a solution of carbene **1b** (100 mg, 0.3 mmol) in benzene-d_6 (0.3 mL). The resulting mixture was stirred at room temperature, and the progress of the reaction was monitored by ^{31}P NMR spectroscopy. Ylide **9** was observed and characterized by NMR spectroscopy, but then it rapidly evolved to afford olefin **10**, which was obtained after evaporation of the solvent as an orange-red oil.

9: ^{31}P NMR (C$_6$D$_6$) δ 54.2; ^{1}H NMR (C$_6$D$_6$) δ 0.1 (s, 9 H), 0.42 (s, 9 H), 1.26–1.34 (m, 25 H), 3.89–4.08 (m, 4 H), 4.97 (s, 1 H), 6.08 (s, 1 H); ^{13}C NMR (C$_6$D$_6$) δ −3.33 (s), −4.38 (s), 10.8 (d, $^1J_{CP}$ = 162 Hz), 22.9–25.1 (m), 46.5 (d, $^2J_{CP}$ = 6 Hz), 48.0 (d, $^2J_{CP}$ = 6 Hz), 109.4 (d, $^3J_{CP}$ = 10 Hz), 162.9 (d, $^2J_{CP}$ = 13 Hz).

10: ^{31}P NMR (C$_6$D$_6$) δ 32.6; ^{1}H NMR (C$_6$D$_6$) δ 0.16 (s, 9 H), 0.24 (s, 9 H), 1.16–1.35 (m, 25 H), 3.36–3.53 (m, 4 H), 4.64 (d, 1 H, $^2J_{HH}$ = 0.5 Hz), 4.94 (d, 1 H, $^2J_{HH}$ = 0.5 Hz); ^{13}C NMR (C$_6$D$_6$) δ −2.3 (s), −2.1 (s), 22.9–24.5 (m), 45.5 (d, $^2J_{CP}$ = 5 Hz), 46.4 (d, $^2J_{CP}$ = 5 Hz), 104.5 (s), 166.9 (s); MS [(M + 2) − SiMe$_3$] 361.2.

Supporting Information Available: General experimental methods; computational details; Cartesian coordinates of all optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) (a) Kolodyazhnyi, O. I.; Kykhar, V. P. *Russ. Chem. Rev.* **1991**, *60*, 391. (b) Kolodyazhnyi, O. I.; Golokhov, D. B.; Boldeskul, I. E. *Tetrahedron Lett.* **1989**, *30*, 2445.
(27) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530.