

# Theoretical Studies of NMR Chemical Shifts and Vibrational Frequencies in $\lambda^3$ -Phosphaalkynes $\text{P}\equiv\text{C}-\text{R}^\dagger$

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A range of  $\lambda^3$ -phosphaalkynes  $\text{P}\equiv\text{C}-\text{R}$  ( $\text{R} = \text{F}, \text{Cl}, \text{O}^-, \text{OLi}, \text{OH}, \text{OSiMe}_3, \text{S}^-, \text{SLi}, \text{SH}, \text{Me}, \text{SiMe}_3, \text{H}$ )<sup>1</sup> has been geometry-optimized at the HF, MP2, and CCSD(T) level of theory. Vibrational frequencies as well as <sup>31</sup>P and <sup>13</sup>C NMR chemical shifts were calculated and compared to experimental values of the large variety of  $\lambda^3$ -phosphaalkynes prepared over several years via differing synthetic routes. With a few obvious exceptions, a good agreement of calculated and experimental parameters was found. This also opens up the possibility to make predictions on spectroscopic data of compounds not yet synthesized or fully characterized, e.g., PCOSiMe<sub>3</sub> and PCSH. The bonding situation especially of the negatively charged species  $\text{P}\equiv\text{C}-\text{O}^-$  and  $\text{P}\equiv\text{C}-\text{S}^-$  was studied via NBO analyses to determine the degree of phosphaalkyne and heterocumulene contributions to the mesomeric anions.

## Introduction

The first compound containing a triple bond between phosphorus and carbon, phosphaethyne  $\text{H}-\text{C}\equiv\text{P}$ , was observed by Gier in 1961 by passing phosphine through a rotating arc struck between graphite electrodes.<sup>2</sup> This phosphaalkyne is highly unstable and polymerizes readily even at temperatures below  $-120^\circ\text{C}$ . 20 years later, with the synthesis of the first thermally stable compound with a  $\text{P}\equiv\text{C}$  triple bond, 2,2-dimethylpropylidynephosphane, by Becker,<sup>3</sup> a rapid development in this as yet scarcely studied field of  $\lambda^3$ -phosphaalkynes began. The results of these investigations on derivatives typically with bulky substituents are summarized in several reviews.<sup>4–8</sup>

Present research is being focused on the chemistry of heteroatom-substituted  $\lambda^3$ -phosphaalkynes, specifically with the preparation and properties of *N,N*-substituted aminomethylidynephosphanes.<sup>9–11</sup> Whereas relatively unstable fluoro-, chloro-, or (trimethylsilyl)methylidynephosphane have been obtained via elimination of hydrogen halide or chlorotrimethylsilane by Nixon,<sup>12</sup> Denis,<sup>13</sup> Appel,<sup>14</sup> and others, Becker et al.

published the syntheses of the surprisingly stable anions  $\text{P}\equiv\text{C}-\text{O}^-$  and  $\text{P}\equiv\text{C}-\text{S}^-$  from lithium bis(trimethylsilyl)phosphanide and the esters of carbonic or thiocarbonic acid, respectively.<sup>15–17</sup> The preparation of a cationic, phosphonium substituted  $\lambda^3$ -phosphaalkyne has recently been achieved by Grützmacher.<sup>18</sup>

Only a few chemical properties of the  $\lambda^3$ -phosphaalkyne  $(\text{dme})_2\text{Li}-\text{O}-\text{C}\equiv\text{P}$  have been studied in detail so far. In solid bis(1,2-dimethoxyethane-*O,O'*)lithoxymethylidynephosphane monomers, molecules with almost linear  $\text{P}-\text{C}-\text{O}-\text{Li}$  fragments are present, with the lithium atom in this neutral complex coordinated to two chelating 1,2-dimethoxyethane ligands.<sup>15</sup> The thio derivative, however, has an ionic structure with triply chelated  $[(\text{dme})_3\text{Li}]^+$  cations and isolated, linear  $\text{P}\equiv\text{C}-\text{S}^-$  anions.<sup>16</sup> The two structures are shown in Figure 1. Compared to the <sup>31</sup>P NMR data of most of the other  $\lambda^3$ -phosphaalkynes, with chemical shifts ranging between +96 for the trimethylsilyl<sup>14</sup> and  $-207$  ppm for the fluoro derivative,<sup>14</sup> the <sup>31</sup>P nucleus in lithoxymethylidynephosphane shows an extreme high-field resonance at  $\delta = -384.2$  ppm.<sup>15</sup> It is still unresolved whether

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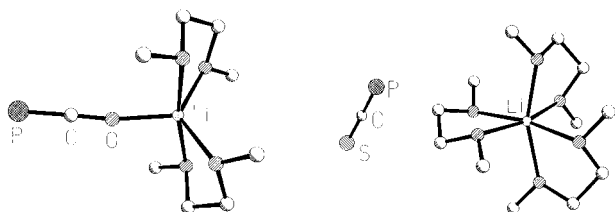
<sup>†</sup> Dedicated to Prof. Warren R. Roper on the occasion of his 60th birthday.

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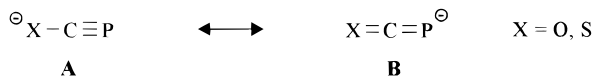
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**Figure 1.** Comparison of X-ray structures for PCOLi(dme)<sub>2</sub> and PCS<sup>-</sup>[Li(dme)<sub>3</sub>]<sup>+</sup>.

### Scheme 1



the protonation of the P≡C–O<sup>-</sup> anion leads to hydroxymethylidynephosphane with a different, but very similar <sup>31</sup>P chemical shift of –392.8 ppm.<sup>15</sup> PCOH could neither be isolated nor be characterized by proton NMR spectroscopy.<sup>19</sup>

The striking stability of some heteroatom-substituted phosphalkynes such as PCOLi and PCSLi is mostly explained through an electronic effect rather than steric hindrance of nucleophilic or electrophilic attack to phosphorus or carbon, respectively, as described for the analogous derivatives with bulky alkyl or aryl substituents. This effect would be more important if in solution the compounds are mostly dissociated into solvated lithium cations and P≡C–O<sup>-</sup> or P≡C–S<sup>-</sup> anions. Furthermore, these anions could be formulated as mesomeric species between heteroalkynes or pseudohalides<sup>20,21</sup> (A) and heterocumulenes (B) as proposed by Jäger and Köhler.<sup>22</sup> Along with the study of the chemical behavior of such compounds, theoretical calculations should be able to decide which of the structures are preferable when discussing these systems.

On the basis of quantum chemical calculations, both anions have been predicted to be stable gas-phase species by Pyykkö and Zhao<sup>23</sup> before being synthesized as stable solids.<sup>17</sup> Earlier theoretical work on the bonding situation claim that for some neutral compounds PCR<sup>1</sup> (e.g. R = H, CH<sub>3</sub>, NH<sub>2</sub>, F, Cl) the system is best described as a phosphalkyne with a P≡C triple bond.<sup>24</sup> Only a weak sensitivity of the P≡C bond length to the substituent at the carbon atom is found.<sup>25</sup> In a microreview, Klapötke compared the PCS<sup>-</sup> anion to several isoelectronic species of CO<sub>2</sub> and CS<sub>2</sub> and concluded that although the CS bond is rather short, the anion is still best formulated as a phosphalkyne rather than as a cumulene.<sup>20</sup>

In this paper we describe ab initio calculations on a series of model compounds P≡C–R including analyses concerned with the bonding situation, NMR as well as vibrational spectra and, if available, comparisons with experimental data.

### Computational Details

Unless stated otherwise, all calculations were performed with the GAUSSIAN94<sup>26</sup> program series including the built-in NBO<sup>27</sup> routines. Geometry optimizations were performed on each of the model compounds P≡C–R (R = F, Cl, O<sup>-</sup>, OLi, OH, OSiMe<sub>3</sub>, S<sup>-</sup>, SLi, SH,

Me, SiMe<sub>3</sub>, H) with linear PCR fragments using gradient techniques. The less important geometric parameters in the peripheral methyl groups of R = OSiMe<sub>3</sub> and SiMe<sub>3</sub> were not refined and kept in local C<sub>3v</sub> symmetry (the geometry optimization and frequency analysis of PCME required several months of CPU runtime on a 16-processor SGI/R10000 super computer). Stationary points were confirmed by frequency analysis. Starting at the HF level, electron correlation was introduced by second-order Møller–Plesset (MP2) perturbation<sup>28</sup> and coupled cluster (CCSD(T)) theory,<sup>29</sup> keeping the orbital space fully active. For the compounds PCSiMe<sub>3</sub> and PCOSiMe<sub>3</sub> CCSD calculations were not feasible due to the high computational demands. For PCOH, PCOLi, PCSH, and PCSLi the geometries were also optimized without restriction to a linear PCR fragment at the MP2 level of theory starting at a nonplanar geometry. The geometries were optimized using valence-modified triple-ζ basis sets (AUG-CC-PVTZ) with the following contractions: (6s,3p,1d) → [5s,3p,1d] for hydrogen, (11s,6p,2d) → [7s,4p,2d] for carbon, (11s,6p,2d) → [6s,4p,2d] for oxygen and fluorine, (16s,10p,3d) → [9s,6p,3d] for silicon, and (16s,10p,3d) → [7s,6p,3d] for phosphorus, sulfur, and chlorine. GIAO-SCF<sup>30</sup> and GIAO-MP2 NMR chemical shifts<sup>31</sup> were calculated using the ACESII<sup>32</sup> program system together with the AUG-CC-PVTZ basis set with and without f functions for the second- and third-row elements, i.e., the following contractions were used: (6s,3p,2d) → [4s,3p,2d] for hydrogen,<sup>33</sup> (11s,6p,3d,2f) → [5s,4p,3d,2f] for the second-row elements,<sup>33,34</sup> and (16s,10p,3d,2f) → [6s,5p,3d,2f] for the third-row elements.<sup>35</sup> For lithium a modified Widmark–Malmqvist–Roos general contraction scheme<sup>36</sup> {(14s,4p,1d) → [8s,4p,1d]} was used in the geometry optimizations and a standard 6-311++G(2D,2P) basis<sup>37</sup> was used in all NMR calculations. All NMR chemical shifts are listed in ppm downfield from tetramethylsilane (<sup>13</sup>C) or 85% phosphoric acid (<sup>31</sup>P) on the δ scale. For converting absolute shieldings into NMR chemical shifts Δσ values of 328.4<sup>38</sup> and 188.1 ppm<sup>39</sup> are used for 85% phosphoric acid (<sup>31</sup>P) and tetramethylsilane (<sup>13</sup>C), respectively. In Table 5 PCH was used as standard at –32 ppm.

Potential energy diagrams for the bending of the PCX angle in PCF, PCCl, PCO<sup>-</sup>, and PCS<sup>-</sup> were calculated at the MP2 level of theory using GAUSSIAN94 and the valence-modified triple-ζ basis sets. The PCX angle was varied between 120 and 180° while all other parameters were kept at the values obtained through the geometry optimizations with linear PCX fragments.

To study the bonding situation in more detail natural localized molecular orbitals (NLMO)<sup>40</sup> based on natural bond orbitals (NBO)<sup>27</sup>

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**Table 1.** Experimental and Calculated Bond Lengths (pm) of  $\lambda^3$ -Phosphaalkynes<sup>a</sup>

| compound                             | P=C   |       |          |                    | C-X   |       |          |                    |
|--------------------------------------|-------|-------|----------|--------------------|-------|-------|----------|--------------------|
|                                      | HF    | MP2   | CCSD(T)  | exp.               | HF    | MP2   | CCSD(T)  | exp.               |
| P=C-F                                | 151.7 | 156.9 | 156.1    | 154.1 <sup>b</sup> | 125.4 | 128.2 | 128.4    | 128.5 <sup>b</sup> |
| P=C-Cl                               | 151.8 | 157.4 | 156.3    | 155.4 <sup>c</sup> | 165.2 | 165.8 | 166.7    | 163.5 <sup>c</sup> |
| P=C-O <sup>-</sup>                   | 162.3 | 163.4 | 163.9    | 155.5 <sup>d</sup> | 116.5 | 121.1 | 120.4    | 119.8 <sup>d</sup> |
| P=C-O-Li <sup>e</sup>                | 157.5 | 161.1 | 160.7    | —                  | 120.5 | 123.8 | 123.8    | —                  |
| P=C-O-H <sup>f</sup>                 | 152.5 | 157.1 | 156.7    | —                  | 128.6 | 131.4 | 131.5    | —                  |
| P=C-O-SiMe <sub>3</sub> <sup>g</sup> | 153.3 | 158.1 | <i>h</i> | —                  | 126.3 | 128.8 | <i>h</i> | —                  |
| P=C-S <sup>-</sup>                   | 157.0 | 161.7 | 161.0    | 155.5 <sup>i</sup> | 163.9 | 164.0 | 164.9    | 162.0 <sup>i</sup> |
| P=C-S-Li <sup>j</sup>                | 155.5 | 161.0 | 159.9    | —                  | 165.8 | 164.9 | 166.5    | —                  |
| P=C-S-H <sup>k</sup>                 | 152.4 | 157.2 | 156.7    | —                  | 170.2 | 171.2 | 171.6    | —                  |
| P=C-Me <sup>l</sup>                  | 152.1 | 156.9 | 156.2    | 154.4 <sup>m</sup> | 146.5 | 146.6 | 147.3    | 146.5 <sup>m</sup> |
| P=C-SiMe <sub>3</sub> <sup>n</sup>   | 152.5 | 157.8 | <i>h</i> | —                  | 187.5 | 186.3 | <i>h</i> | —                  |
| P=C-H                                | 151.4 | 156.2 | 155.6    | 154.2 <sup>o</sup> | 106.0 | 106.8 | 106.7    | 106.7 <sup>o</sup> |

<sup>a</sup> The P=C-R angle is 180°. Experimental data are from X-ray structure analysis (X-ray), electron diffraction (ED), or microwave spectroscopy (MW). <sup>b</sup> See ref 12b (MW). <sup>c</sup> See ref 41 (MW). <sup>d</sup> P=C-O, 178.5°; see ref 15 (X-ray). <sup>e</sup> OLi, 184.5 (HF), 194.6 (MP2), and 189.1 pm (CCSD(T)); COLi, 79.6 (HF), 72.6 (MP2), 74.6° (CCSD(T)). <sup>f</sup> OH, 94.5 (HF), 96.2 (MP2), and 95.9 pm (CCSD(T)); COH, 111.6 (HF), 109.1 (MP2), and 109.2° (CCSD(T)). <sup>g</sup> OSi, 170.6 (HF) and 174.1 pm (MP2); COSi, 127.0 (HF) and 118.9° (MP2). <sup>h</sup> Not performed due to high computational demands. <sup>i</sup> P=C-S, 178.9°; see ref 16 (X-ray). <sup>j</sup> SLi, 230.3 (HF), 239.2 (MP2), and 232.9 pm (CCSD(T)); CSLi, 60.7 (HF), 56.6 (MP2), and 58.1° (CCSD(T)). <sup>k</sup> SH, 133.2 (HF), 133.3 (MP2), and 133.3 pm (CCSD(T)); CSH, 97.4 (HF), 95.2 (MP2), and 95.9° (CCSD(T)). <sup>l</sup> CH, 108.2 (HF), 108.7 (MP2), and 108.8 pm (CCSD(T)); CCH, 110.4 (HF), 110.6 (MP2), and 110.5° (CCSD(T)). <sup>m</sup> See ref 42 (MW). <sup>n</sup> SiC, 189.0 (HF) and 188.9 pm (MP2); CSiC, 108.0 (HF) and 107.4° (MP2). <sup>o</sup> See ref 43 (MW).

**Table 2.** Comparison of Bond Lengths (pm) and Angles (deg) as Well as Absolute Shieldings for Structures Optimized with and without (nl: Nonlinear) Restriction to a Linear PCR Fragment<sup>a</sup>

| compound      | PC    | PCX   | CX    | CXH/Li | XH/Li | tors. <sup>b</sup> | $\sigma(^{31}\text{P})$ HF | $\sigma(^{31}\text{P})$ MP2 | $\sigma(^{13}\text{C})$ HF | $\sigma(^{13}\text{C})$ MP2 |
|---------------|-------|-------|-------|--------|-------|--------------------|----------------------------|-----------------------------|----------------------------|-----------------------------|
| P=C-O-Li      | 161.1 | 180.0 | 123.8 | 72.6   | 194.6 | —                  | 699.2                      | 754.6                       | 1.7                        | 33.2                        |
| P=C-O-Li (nl) | 161.9 | 167.0 | 123.2 | 70.9   | 197.3 | 0.0                | 698.2                      | 746.5                       | -3.7                       | 30.2                        |
| P=C-O-H       | 157.1 | 180.0 | 131.4 | 109.1  | 96.2  | —                  | 600.7                      | 678.6                       | 31.6                       | 46.7                        |
| P=C-O-H (nl)  | 157.0 | 176.5 | 131.2 | 109.6  | 96.1  | 180.0              | 601.4                      | 679.8                       | 32.2                       | 47.0                        |
| P=C-S-Li      | 161.0 | 180.0 | 164.9 | 56.6   | 239.2 | —                  | 405.6                      | 510.9                       | -45.6                      | 14.6                        |
| P=C-S-Li (nl) | 161.3 | 170.7 | 164.8 | 57.9   | 234.8 | 0.0                | 406.8                      | 505.0                       | -53.1                      | 13.3                        |
| P=C-S-H       | 157.2 | 180.0 | 171.2 | 95.2   | 133.3 | —                  | 277.6                      | 481.0                       | 23.6                       | 32.8                        |
| P=C-S-H (nl)  | 157.0 | 175.7 | 170.9 | 95.5   | 133.0 | 180.0              | 276.0                      | 481.2                       | 24.1                       | 32.9                        |

<sup>a</sup> All values in ppm. NMR chemical shifts can be calculated according to the instructions given in Table 4. <sup>b</sup> Optimized torsion angle PCXH or PCXLi for the nonlinear structures.

analyses were computed for all species with the structures optimized at the coupled cluster level. The set of NBOs automatically found by the NBO program for all  $\lambda^3$ -phosphaalkynes include one  $\sigma$  and two  $\pi$  bonds between phosphorus and carbon and a single bond from carbon to the group R. In a second step the systems were allowed to delocalize.

## Results and Discussion

A comparison between measured and theoretical structural data is shown in Table 1. Except for the negatively charged species the coupled cluster values are in good agreement with experimental results. For the species PCO<sup>-</sup>/PCOLi and PCS<sup>-</sup>/PCSLi the gas phase structures are not directly comparable with the solid state results because of the additional solvent molecules present when looking at the experimental data. In these cases the calculated PC and CO bond distances are well below the measured values, suggesting that interaction with other ions or solvent molecules in the solid state will cause a widening of the interatomic distances. The influence of basis sets and the applied computational method on bond lengths and angles has been extensively studied for the parent compound HCP and for some substituted phosphaalkynes.<sup>44-46</sup>

Veszprémi et al. showed that if one would not constrain the PCX angle to 180°, the structure of minimum energy for the

species PCOLi and PCSLi features a four membered PCXLi ring with PCX angles of 165 and 170°, respectively.<sup>47</sup> However, in solution we expect that the lithium cation is only weakly coordinated to the corresponding phosphaalkyne anion and the PCX angle should be close to 180°. When comparing the influence of the lithium cation being coordinated to the phosphaalkyne anion PCO<sup>-</sup> or PCS<sup>-</sup> it is obvious that PC and CX bond lengths are significantly more affected for X = O than they are for X = S. This can be explained by a particularly good interaction of the negatively charged oxygen atom in PCO<sup>-</sup> with the two  $\pi$ (CP) bonds while in PCOLi, according to the HSAB concept<sup>48</sup> the hard oxygen anion should interact well with the similarly hard lithium cation. For the sulfur analogues both interactions should be expected to be much weaker and thus, the effect on all bonding parameters will be smaller (see also NBO analysis).

When the geometries of PCOH, PCOLi, PCSH, and PCSLi were refined without any restrictions, the structures stayed essentially planar with PCX angles converging to 176.5, 167.0, 175.7, and 170.7° (Table 2, Figure 2). Furthermore, the difference in bond lengths between linear and bent structures are mostly less than 0.3 pm (less than 0.8 pm for PCOLi) with the exception of the more ionic interactions between lithium and the two chalcogene atoms O and S which increase by 2.7 (LiO) and decrease by 4.4 (LiS) to 197.3 and 234.8 pm,

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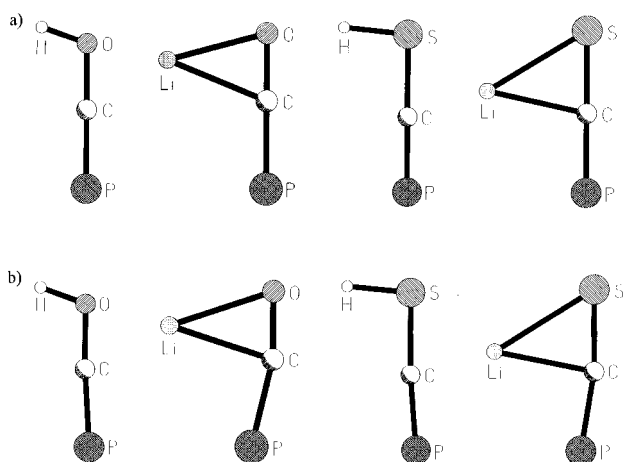
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**Table 3.** Vibrational Data of  $\lambda^3$ -Phosphaalkynes<sup>a</sup>

| compound                | $\delta(\text{PCX})$ |                        |          |                    | $\nu(\text{CX})$ |            |          |                     | $\nu(\text{PC})$ |              |          |                   |
|-------------------------|----------------------|------------------------|----------|--------------------|------------------|------------|----------|---------------------|------------------|--------------|----------|-------------------|
|                         | HF                   | MP2                    | CCSD(T)  | exp.               | HF               | MP2        | CCSD(T)  | exp.                | HF               | MP2          | CCSD(T)  | exp.              |
| P≡C-F                   | 453.4                | 361.8(8)               | 347.0    | 375 <sup>b</sup>   | 884.0            | 754.2(39)  | 768.2    | 780 <sup>b</sup>    | 1850.8           | 1665.1(313)  | 1669.6   | 1671 <sup>b</sup> |
| P≡C-Cl                  | 345.5                | 227.4(9)               | 267.2    | 303 <sup>c</sup>   | 611.7            | 550.5(17)  | 550.4    | 574 <sup>c</sup>    | 1648.0           | 1427.9(117)  | 1458.8   | 1477 <sup>c</sup> |
| P≡C-O <sup>-</sup>      | 568.5                | 477.7(8)               | 474.5    | 486                | 842.5            | 798.3(2)   | 786.2    | <i>d</i>            | 1954.9           | 1827.8(1077) | 1803.7   | 1763 <sup>e</sup> |
| P≡C-O-Li                | 545.1                | 446.7(8)               | 444.6    | —                  | 927.5            | 816.8(34)  | 824.6    | —                   | 1831.4           | 1767.4(713)  | 1720.7   | —                 |
| P≡C-O-H                 | 479.9                | 378.0(4)               | 376.1    | —                  | 898.7            | 779.3(38)  | 786.7    | —                   | 1802.3           | 1674.9(287)  | 1651.0   | —                 |
| P≡C-O-SiMe <sub>3</sub> | 494.3 <sup>f</sup>   | 429.9(29) <sup>f</sup> | <i>g</i> | —                  | 1008.9           | 857.9(339) | <i>g</i> | —                   | 1792.1           | 1676.7(721)  | <i>g</i> | —                 |
| P≡C-S <sup>-</sup>      | 403.7                | 338.6(14)              | 334.9    | 369                | 629.4            | 586.4(22)  | 579.9    | 590 <sup>h</sup>    | 1433.7           | 1374.3(626)  | 1341.1   | <i>d, h</i>       |
| P≡C-S-Li                | 381.3                | 318.0(14)              | 313.1    | —                  | 625.1            | 605.4(123) | 579.2    | —                   | 1478.1           | 1370.6(399)  | 1353.6   | —                 |
| P≡C-S-H                 | 351.6                | 277.0(11)              | 280.3    | —                  | 589.3            | 537.4(2)   | 535.4    | —                   | 1594.8           | 1463.2(40)   | 1426.1   | —                 |
| P≡C-Me                  | 351.8                | 289.5(12)              | 280.0    | 316 <sup>i</sup>   | 790.3            | 727.9(0.3) | 729.7    | 750 <sup>i</sup>    | 1714.8           | 1536.1(16)   | 1553.2   | 1543 <sup>i</sup> |
| P≡C-SiMe <sub>3</sub>   | 361.0                | 304.5(17)              | <i>g</i> | —                  | 470.1            | 441.2(18)  | <i>g</i> | —                   | 1615.5           | 1370.5(31)   | <i>g</i> | 1572 <sup>j</sup> |
| P≡C-H                   | 824.3                | 660.1(74)              | 642.2    | 672 <sup>b,k</sup> | 3525.0           | 3392.3(15) | 3387.9   | 3217 <sup>b,k</sup> | 1458.5           | 1236.4(0)    | 1271.7   | 1278              |

<sup>a</sup> All bending ( $\delta$ ) and stretching ( $\nu$ ) frequencies in  $\text{cm}^{-1}$ ; intensities at the MP2 level in  $\text{km mol}^{-1}$  are given in parentheses. <sup>b</sup> See ref 51. <sup>c</sup> See ref 52;  $\nu(\text{PC}) = 1460$ .<sup>13</sup> <sup>d</sup> Not assigned due to overlap with solvent bands. <sup>e</sup> See refs 15 and 17. <sup>f</sup> Value of the more intense of two nondegenerate deformations. <sup>g</sup> Not performed due to high computational demands. <sup>h</sup> Earlier published frequencies:  $\nu(\text{CS}) = 747$  and  $\nu(\text{PC}) = 1762$ .<sup>16,17</sup> <sup>i</sup> See ref 53;  $\nu(\text{PC}) = 1559$ .<sup>13,54</sup> <sup>j</sup> See ref 13. <sup>k</sup>  $\delta(\text{PCH}) = 671$ ,  $\nu(\text{CH}) = 3180$ ,  $\nu(\text{PC}) = 1265$ .<sup>2</sup> <sup>l</sup>  $\nu(\text{PC}) = 1267$ .<sup>13</sup>



**Figure 2.** Comparison of geometries for PCOH, PCOLi, PCSH, and PCSLi at CCSD(T) (a) and without any geometry restrictions at the MP2 level (b).

respectively. Starting with the linear optimized geometry, energies for a variety of PCX angles were calculated for  $\text{PCO}^-$ ,  $\text{PCS}^-$ , PCF, and PCCl to finally result in potential energy diagrams with minima at  $180^\circ$ . Curves were fitted via 6th-order polynomial regression and the second energy derivatives with respect to the deviation of the bending angles from linearity were calculated to be 109, 85, 67, and  $56 \text{ J mol}^{-1} \text{ deg}^{-2}$  at  $180^\circ$ . This confirms that these species are linear in the gas phase as expected, and only coordination leads to bent structures. The potential curves also show that the ability to bend is  $\text{PCCl} > \text{PCF} > \text{PCS}^- > \text{PCO}^-$ . This trend correlates nicely with what one would expect from the ability of the X ligand to donate  $\pi$  electrons. As earlier work shows the potential energy surface of FCP can have several energy minima depending on the method applied.<sup>49,50</sup> However, the species of absolutely lowest energy is always the linear one.

In most cases electron correlation contributions to bond distances cannot be neglected and the MP2 approximation often performs well compared to the more computer time-demanding coupled cluster method.

**Frequency Analysis.** The vibrational data are shown in Table 3. Again, the coupled cluster method yields results in very good

agreement with the experiment, without the values being multiplied with an additional scaling factor. The remaining small differences can be attributed to effects of anharmonicity, basis set incompleteness, insufficient treatment of electron correlation, and solvation. However, the PC stretching frequency for PCF, PCCl, PCMe, and PCH is in very close agreement with the experimental values. We may therefore predict if the solvated PCOLi or PCSLi species measured by IR spectroscopy as Nujol mulls were present in their dissociated ionic forms,  $\text{PCO}^-$  and  $\text{PCS}^-$ , or not. The calculated CCSD(T) results show that the experimental PC stretching frequency for PCOLi lies between the two extreme cases,  $\text{PCO}^-$  and PCOLi. Hence we predict some interaction between  $\text{Li}^+$  and  $\text{PCO}^-$ . It would therefore be interesting to study the influence of solvent effects to the PC stretching frequency. For PCSLi a comparison with experimental data is not possible because the PC stretching frequency at around  $1350 \text{ cm}^{-1}$  overlaps with solvent bands. Furthermore, according to our calculations neither the PC or CS stretching nor the PCS deformation frequency seem to be very sensitive to the lithium atom being coordinated or not, which makes a decision between PCSLi and  $\text{PCS}^-$  based on vibrational data impossible.

The IR intensities at the MP2 level of theory are also listed in Table 3. There is a good quantitative agreement with the measured IR intensities of PCMe,<sup>53</sup> i.e., the dominating bands in the experimental spectrum  $\{\nu(\text{PC}) 1543 \text{ vs. } \delta(\text{CH}_3) 1440 \text{ s and } \delta(\text{PCC}) 316 \text{ cm}^{-1} \text{ vs.}\}$  are also calculated to be the most intense frequencies  $\{1536.1(16), 1485.8(10), 289.5 \text{ cm}^{-1} (12 \text{ km mol}^{-1})\}$  whereas the weak experimental band for the CC stretching at  $750 \text{ cm}^{-1}$  matches the calculation of a corresponding band at  $727.9 \text{ cm}^{-1} (0.3 \text{ km mol}^{-1})$ .

**NMR.** The  $^{31}\text{P}$  and  $^{13}\text{C}$  absolute shieldings are listed in Table 4 at the HF and MP2 level of theory. The  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR chemical shifts can easily be calculated thereof (see footnotes *b* and *c* in Table 4). Again, electron correlation is important, particularly for the  $\sigma(^{31}\text{P})$  values of compounds with small absolute shielding values (positive or small negative chemical shifts) such as  $\text{PCSiMe}_3$  or PCSH, for which HF and MP2 calculations differ by up to 200 ppm. An analogous observation can be made for  $^{13}\text{C}$  absolute shieldings where electron correlation mostly effects species with highly negative values, e.g. the  $\text{PCS}^-$  anion for which results from HF and MP2

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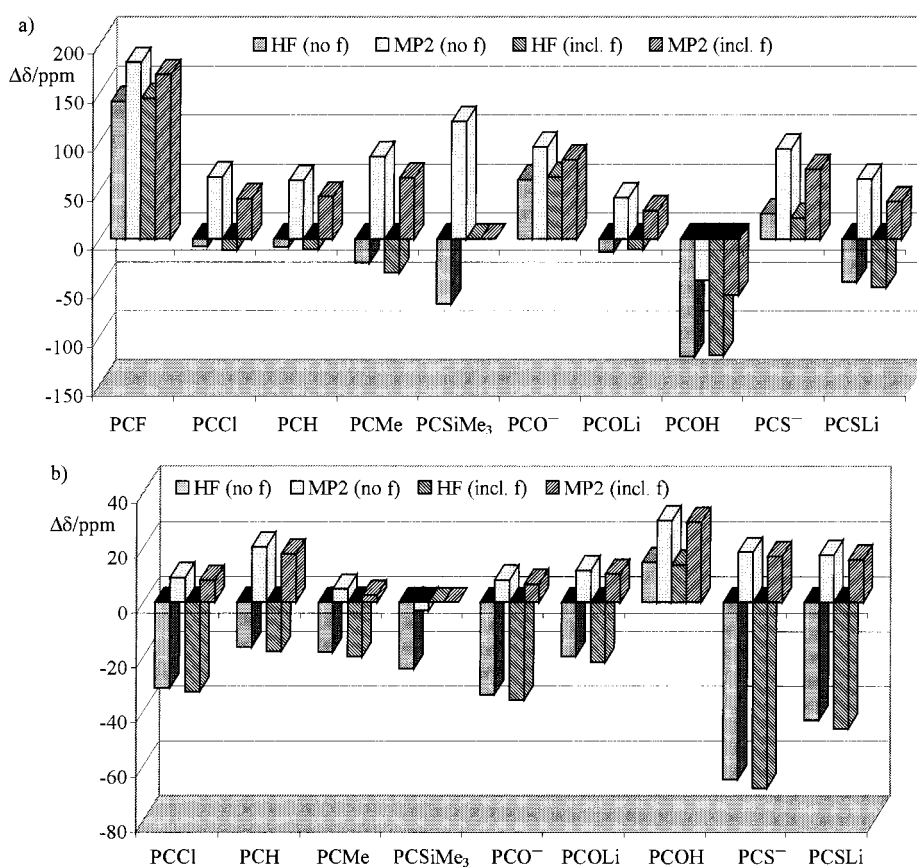
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**Table 4.**  $^{31}\text{P}$  and  $^{13}\text{C}$  Absolute Shieldings of  $\lambda^3$ -Phosphaalkynes without and with f Functions; Calculations Were Carried out for MP2 Optimized Geometries at HF and MP2 Levels of Theory<sup>a</sup>

| compound             | $^{31}\text{P}$ absolute shieldings |          |            |             |                    | $^{13}\text{C}$ absolute shieldings |          |            |             |                    |
|----------------------|-------------------------------------|----------|------------|-------------|--------------------|-------------------------------------|----------|------------|-------------|--------------------|
|                      | HF no f                             | MP2 no f | HF incl. f | MP2 incl. f | exp. <sup>b</sup>  | HF no f                             | MP2 no f | HF incl. f | MP2 incl. f | exp. <sup>c</sup>  |
| $P\equiv C-F$        | 675.8                               | 715.5    | 678.6      | 703.1       | 535 <sup>d</sup>   | 42.9                                | 58.9     | 42.3       | 58.7        | —                  |
| $P\equiv C-Cl$       | 436.3                               | 507.6    | 432.8      | 485.5       | 444 <sup>e</sup>   | 30.5                                | 70.8     | 29.0       | 69.8        | 61.7 <sup>e</sup>  |
| $P\equiv C-O^-$      | 772.9                               | 806.6    | 775.6      | 793.4       | 712.6 <sup>f</sup> | -12.2                               | 29.6     | -14.2      | 28.2        | 21.5 <sup>f</sup>  |
| $P\equiv C-O-Li$     | 699.2                               | 754.6    | 701.3      | 741.5       | —                  | 1.7                                 | 33.2     | -0.3       | 31.9        | —                  |
| $P\equiv C-O-H$      | 600.7                               | 678.6    | 601.7      | 663.7       | 721.2 <sup>f</sup> | 31.6                                | 46.7     | 30.6       | 46.2        | 17.0 <sup>f</sup>  |
| $P\equiv C-O-SiMe_3$ | 632.0                               | 682.3    | g          | g           | —                  | 24.5                                | 49.5     | g          | g           | —                  |
| $P\equiv C-S^-$      | 475.5                               | 541.5    | 470.9      | 520.8       | —                  | -67.5                               | 15.6     | -70.6      | 14.1        | —                  |
| $P\equiv C-S-Li$     | 405.6                               | 510.9    | 400.0      | 487.6       | 449.7 <sup>h</sup> | -45.6                               | 14.6     | -48.8      | 12.8        | -2.1 <sup>h</sup>  |
| $P\equiv C-S-H$      | 277.6                               | 481.0    | 269.9      | 458.5       | —                  | 23.6                                | 32.8     | 22.2       | 31.4        | —                  |
| $P\equiv C-Me$       | 364.1                               | 472.6    | 353.6      | 450.5       | 388.4 <sup>i</sup> | -0.9                                | 22.2     | -2.6       | 19.9        | 17.3 <sup>i</sup>  |
| $P\equiv C-SiMe_3$   | 165.7                               | 352.3    | g          | g           | 232 <sup>j</sup>   | -37.6                               | -16.3    | g          | g           | -13.2 <sup>j</sup> |
| $P\equiv C-H$        | 351.9                               | 420.0    | 349.4      | 403.4       | 360.4 <sup>k</sup> | 13.7                                | 50.2     | 12.2       | 47.7        | 30.1 <sup>k</sup>  |

<sup>a</sup> All values in ppm. The total shielding consists of the diamagnetic and paramagnetic contribution. <sup>b</sup>  $^{31}\text{P}$  absolute shieldings were calculated by adding  $\Delta\sigma = 328.4$  to  $-\delta$ .<sup>38</sup> <sup>c</sup>  $^{13}\text{C}$  absolute shieldings were calculated by adding  $\Delta\sigma = 188.1$  to  $-\delta$ .<sup>39</sup> <sup>d</sup> See ref 12a. <sup>e</sup> See ref 13. <sup>f</sup> See ref 15. <sup>g</sup> Not performed due to high computational demands. <sup>h</sup> See ref 16. <sup>i</sup> See ref 55. <sup>j</sup> See ref 14. <sup>k</sup> See refs 7, 55, and 56.

**Figure 3.** Differences between calculated and experimental  $^{31}\text{P}$  (a) and  $^{13}\text{C}$  (b) absolute shieldings. Values for  $PCSiMe_3$  including f functions were not calculated.

calculations differ by more than 80 ppm. This is due to the presence of a large and negative paramagnetic term at the HF level, on which the contribution from electron correlation is mostly dependent, for the most deshielded atoms such as  $^{31}\text{P}$  in  $PCSiMe_3$  or  $^{13}\text{C}$  in  $PCS^-$ . Also shown in Table 4 are results with and without f functions for the second- and third-row elements. For the absolute shielding tensors f functions are also important, particularly at the MP2 level of theory, as one would expect, but they are not as relevant as electron correlation. The differences between the theoretical and experimental  $^{31}\text{P}$  and  $^{13}\text{C}$  absolute shielding values are compared in Figure 3a and 3b, respectively. As one can see from these figures, the experimental shieldings are—with a few exceptions discussed later—between the HF and the MP2 values. Further calculations

at an even higher level of theory would be expected to partly compensate the effects brought in through simple electron correlation at MP2 as this can also be seen for the geometry optimizations at the CCSD(T) level (see Table 1).

For calculating chemical shifts a suitable reference system is required. Although 85%  $H_3PO_4$  is usually used as a reference for  $^{31}\text{P}$  NMR chemical shift, from a theoretical point of view this is not a suitable system because of important interactions with other  $H_3PO_4$  molecules and  $H_2O$ . We therefore decided to use PCH as a standard, where an accurate experimental  $^{31}\text{P}$  NMR chemical shift is available. Hence, the  $^{31}\text{P}$  chemical shift values for PCH are set to the experimental value of  $-32$  ppm (Table 5). On one hand, this means that all calculations will also include the PCH characteristics. On the other hand, at least

**Table 5.**  $^{31}\text{P}$  NMR Chemical Shifts of  $\lambda^3$ -Phosphaalkynes<sup>a</sup>

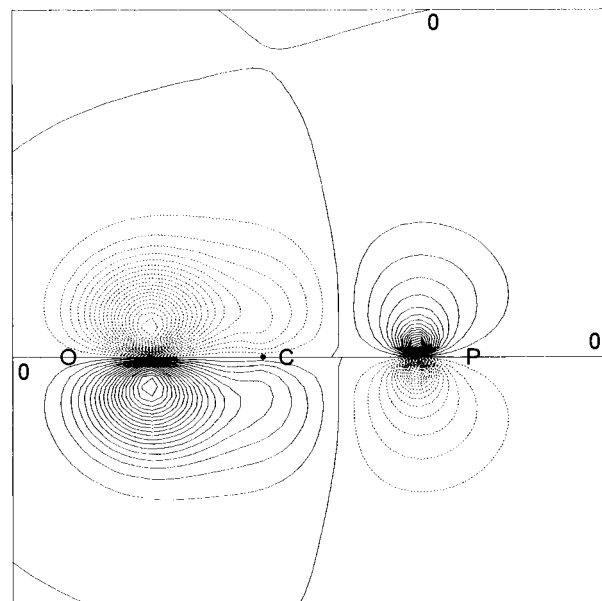
| compound  | $^{31}\text{P}$ NMR chemical shifts |          |            |             |                     |
|---|-------------------------------------|----------|------------|-------------|---------------------|
|   | HF no f                             | MP2 no f | HF incl. f | MP2 incl. f | exp.                |
| $\text{P}\equiv\text{C}-\text{F}$               | -356.0                              | -327.5   | -361.2     | -331.7      | -207 <sup>c</sup>   |
| $\text{P}\equiv\text{C}-\text{Cl}$              | -116.4                              | -119.6   | -115.4     | -114.0      | -116 <sup>d</sup>   |
| $\text{P}\equiv\text{C}-\text{O}^-$             | -453.0                              | -418.6   | -458.2     | -421.9      | -384.2 <sup>e</sup> |
| $\text{P}\equiv\text{C}-\text{O}-\text{Li}$     | -379.4                              | -366.6   | -383.9     | -370.0      |                     |
| $\text{P}\equiv\text{C}-\text{O}-\text{H}$      | -280.8                              | -290.6   | -284.4     | -292.2      | -392.8 <sup>e</sup> |
| $\text{P}\equiv\text{C}-\text{O}-\text{SiMe}_3$ | -312.1                              | -294.3   | <i>f</i>   | <i>f</i>    | -                   |
| $\text{P}\equiv\text{C}-\text{S}^-$             | -155.6                              | -153.5   | -153.5     | -149.4      | -121.3 <sup>g</sup> |
| $\text{P}\equiv\text{C}-\text{S}-\text{Li}$     | -85.8                               | -122.9   | -82.7      | -116.2      |                     |
| $\text{P}\equiv\text{C}-\text{S}-\text{H}$      | 42.3                                | -93.0    | 47.4       | -87.0       | -                   |
| $\text{P}\equiv\text{C}-\text{Me}$              | -44.2                               | -84.6    | -36.2      | -79.1       | -60.0 <sup>h</sup>  |
| $\text{P}\equiv\text{C}-\text{SiMe}_3$          | 154.2                               | 35.7     | <i>f</i>   | <i>f</i>    | 96 <sup>i</sup>     |
| $\text{P}\equiv\text{C}-\text{H}$               | -32.0                               | -32.0    | -32.0      | -32.0       | -32.0               |

<sup>a</sup> All values in ppm were calculated from the absolute shieldings of Table 4 with PCH as an internal standard for every basis set and method set to -32.0 ppm. <sup>c</sup> See ref 12a. <sup>d</sup> See ref 13. <sup>e</sup> See ref 15. <sup>f</sup> Not performed due to high computational demands. <sup>g</sup> See ref 16. <sup>h</sup> See ref 55. <sup>i</sup> See ref 14. <sup>j</sup> See ref 7, 55, and 56.

for the  $^{31}\text{P}$  chemical shifts, most of the differences between calculated and experimental values that are due to an incomplete description of the PC triple bond by the chosen basis sets and the methods applied are likely to be eliminated that way.

Except for a few compounds which we will discuss in detail, the deviations are what one expects for the theoretical method applied. However, the error in the  $^{31}\text{P}$  chemical shift of PCF is too large to be attributed to basis set effects or the electron correlation procedure applied. For PCF the HF and MP2  $^{31}\text{P}$  chemical shifts are not too different, suggesting that the MP2 method converges well and therefore a coupled cluster treatment would not lead to significantly different results. IGLO calculations of phosphorus chemical shifts by Kutzelnigg et al. have already resulted in  $\delta$  values of -43 and -344 ppm for  $\text{HP}=\text{CF}_2$  and PCF, respectively.<sup>57</sup> Although there is no doubt about the existence of PCF, since this compound is sufficiently characterized by other spectroscopic methods,<sup>12,51</sup> in agreement with the author of the experimental work we can see a certain likelihood of the  $^{31}\text{P}$  chemical shift being assigned wrongly,<sup>58</sup> most likely due to a peak fold back, and suggest the experiment be repeated. This would also explain the assignment of the correct PF coupling constant in agreement with the  $^{19}\text{F}$  NMR spectrum. To confirm the theoretical results we have calculated the  $^{31}\text{P}$  NMR chemical shift of  $\text{HP}=\text{CF}_2$  and  $\text{H}_2\text{P}-\text{CF}_3$ , two compounds also present in the original  $^{31}\text{P}$  NMR spectrum of PCF. At the MP2 level of theory (no f functions) chemical shifts of -78 and -114 ppm are in very good agreement with the experimental values of -62 and -122 ppm, respectively, and indicate the high reliability of the calculated  $^{31}\text{P}$  shift for PCF at about -350 ppm.

For PCOLi and PCSLi the measured  $^{31}\text{P}$  chemical shift values are between the two extreme cases of the completely dissociated species  $\text{PCX}^-$  and  $\text{PCXLi}$  ( $\text{X} = \text{O}, \text{S}$ ) (Table 5). This again suggests some interaction of the Li atom with oxygen in  $\text{PCO}^-$  or sulfur in  $\text{PCS}^-$  in the solvent. If one compares the experimental value with the absolute shieldings (Table 4, Figure



**Figure 4.** Contour plot of the natural localized molecular orbital (NLMO) for the delocalization of an oxygen lone pair in the anion  $\text{PCO}^-$  generated with the program MOLDEN.<sup>60</sup> Full lines designate positive and dotted lines negative values of the orbital changing in steps of 0.02.

3a) it is likely that in solution PCOLi is the preferred species, whereas  $\text{PCS}^-$  and  $\text{PCSLi}$  seem to be similarly favored.

The  $^{31}\text{P}$  chemical shift of PCOH is (beside that of PCF) the other value in disagreement with the experimentally obtained data. This compound has been tentatively assigned an experimental  $\delta(^{31}\text{P})$  value of -392.8 ppm,<sup>15</sup> which is only 8.6 ppm different from the chemical shift recorded for PCOLi. Since PCOH is not well characterized<sup>19</sup> and, as shown in this paper, coordination of lithium to the  $\text{PCO}^-$  anion changes the chemical shift by about 50 ppm, we propose that due to influence of the solvent the lithium compound PCOLi and not PCOH has actually been detected at -392.8 ppm and suggest further experimental work.<sup>19</sup> PCOH itself or the probably more stable silylated derivative  $\text{PCOSiMe}_3$  should be expected to have  $^{31}\text{P}$  absolute shieldings  $\sigma$  (between the values calculated at HF and MP2 level of theory) of approximately 630 and 660 ppm (Table 4) converting to chemical shifts of -300 and -330 ppm, respectively. The only other compound shown in Table 5 for which there are no published NMR shifts available, PCSH, is predicted to have a  $\delta(^{31}\text{P})$  value of about -30 ppm.

As for the geometrical parameters discussed earlier, the differences between the NMR chemical shifts calculated for the fully optimized structures and the species optimized with restriction to a linear  $\text{PCX}$  fragment are only minor (Table 2). For PCOH and PCSH the values yielded by the different methods are almost identical, and the differences for  $\delta(^{31}\text{P})$  at the MP2 level of theory are only 8.1 and 5.9 ppm for PCOLi and PCSLi, respectively. Even smaller deviations can be found with 2.9 and 1.3 ppm for the analogous  $\Delta\delta(^{13}\text{C})$  values. Since the phosphorus and carbon chemical shifts discussed in this paper are spread over a total area of more than 500 and 100 ppm, respectively, these differences can be viewed as minor.

**NBO Analysis.** The NBO analysis is summarized in Table 6. The NBO charges basically reflect the Pauling electronegativities of the elements (H, 2.20; C, 2.55; N, 3.04; O, 3.44; P, 2.19; S, 2.58).<sup>59</sup> However, the cumulene-type structure **B** does

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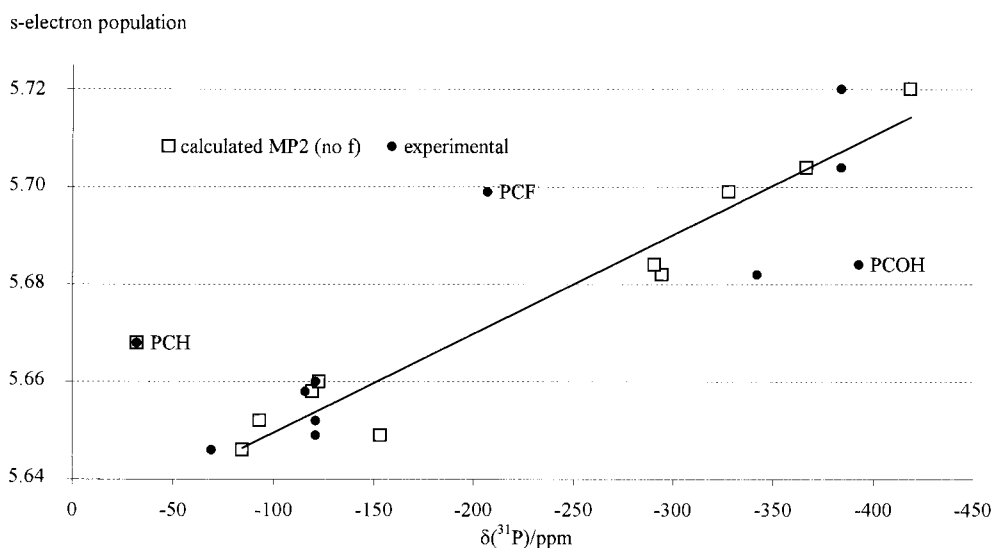
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**Table 6.** Results of the NBO Analyses for  $\lambda^3$ -phosphaalkynes  $P\equiv C-R$  Based on SCF Densities at CCSD(T) Geometries

| compound               | $q(P)^a$ | $q(C)^a$ | $q(X)^a$ | s pop. at P <sup>b</sup> | BO(PC) <sup>c</sup> | BO(CX) <sup>c</sup> | % at P <sup>d</sup> | % at C <sup>d</sup> | % d at C <sup>d</sup> |
|------------------------|----------|----------|----------|--------------------------|---------------------|---------------------|---------------------|---------------------|-----------------------|
| $P\equiv C-F$          | 0.37     | -0.02    | -0.34    | 5.699                    | 2.57                | 0.60                | 1.59                | 1.64                | 4.39                  |
| $P\equiv C-Cl$         | 0.56     | -0.67    | 0.11     | 5.658                    | 2.32                | 1.02                | 2.33                | 1.92                | 4.84                  |
| $P\equiv C-O^-$        | -0.51    | 0.29     | -0.78    | 5.720                    | 1.83                | 1.03                | 4.64                | 9.83                | 1.00                  |
| $P\equiv C-O-Li$       | -0.04    | -0.05    | -0.86    | 5.704                    | 2.28                | 0.91                | 5.23/4.65           | 5.39/7.39           | 2.94/1.83             |
| $P\equiv C-O-H$        | 0.33     | -0.12    | -0.72    | 5.684                    | 2.43                | 0.72                | 2.53                | 3.11                | 2.81                  |
| $P\equiv C-O-SiMe_3^e$ | 0.25     | -0.07    | -0.89    | 5.682                    | 2.48                | 0.72                | 2.73                | 3.33                | 2.42                  |
| $P\equiv C-S^-$        | -0.04    | -0.62    | -0.34    | 5.649                    | 2.28                | 1.12                | 5.95                | 7.02                | 1.61                  |
| $P\equiv C-S-Li$       | 0.26     | -0.89    | -0.32    | 5.660                    | 2.28                | 1.05                | 6.16/6.11           | 5.21/6.38           | 4.33/2.64             |
| $P\equiv C-S-H$        | 0.56     | -0.81    | 0.15     | 5.652                    | 2.31                | 0.97                | 3.44                | 3.38                | 2.46                  |
| $P\equiv C-Me$         | 0.51     | -0.52    | -0.62    | 5.646                    | 2.47                | 1.03                | <i>f</i>            | <i>f</i>            | <i>f</i>              |
| $P\equiv C-SiMe_3^e$   | 0.57     | -1.07    | 1.75     | 5.457                    | 2.42                | 0.52                | <i>f</i>            | <i>f</i>            | <i>f</i>              |
| $P\equiv C-H$          | 0.53     | -0.73    | 0.20     | 5.668                    | 2.48                | 0.78                | —                   | —                   | —                     |

<sup>a</sup> Charges  $q$ . <sup>b</sup> Population of s orbital at phosphorus. <sup>c</sup> Atom-atom net linear bond orders. <sup>d</sup> Percentage from parent NBO after delocalization of the lone pairs with mostly p character of group R based on the NLMO/NPA analyses and participation of d orbitals at the central carbon atom.<sup>40</sup> <sup>e</sup> CCSD(T) calculations were not performed due to high computational effort; MP2 geometries were used instead. <sup>f</sup> Delocalization of CH and SiC bonds can be neglected.

**Figure 5.** Correlation of s electron population (Table 6) at P atom with experimental and calculated  $^{31}P$  NMR chemical shifts (Table 5).

play an important role when discussing the bonding situation of the anionic  $\lambda^3$ -phosphaalkynes  $PCO^-$  and  $PCS^-$ . Even though the oxygen is more electronegative than sulfur, the phosphorus NPA charge is significantly more negative in  $PCO^-$  (-0.51) compared to  $PCS^-$  (-0.04) indicating larger  $\pi$  donation by the oxygen atom and thus a shift from resonance structure **A** to **B**. Indeed, in  $PCXLi$  and  $PCXH$  ( $X = O, S$ ) this effect is diminished as the charges show. This is also evident in the PC bond order (BO) of  $PCO^-$  which is significantly lower than the one in  $PCOLi$  or  $PCOH$ . This bond order effect is less significant in  $PCS^-$ . As expected, the decrease in the PC bond order is accompanied by an increase in the CX bond order.

The same effect can also be seen when NLMOs are formed from NBOs (Table 6). Here, the lone pairs at oxygen in  $PCO^-$  delocalize into hybrids on carbon more extensively (9.82) than the lone pairs of sulfur in  $PCS^-$  (7.02%), while this effect is significantly smaller for  $PCOLi$  (5.39/7.39%) and  $PCSLi$  (5.21/6.38%) and smaller again for the corresponding hydrogen compounds (3.11 and 3.38%). With less than 5% participation in the hybrids involved at carbon, d orbitals do not play an important role in this delocalization process. Figure 4 shows an electron isodensity contour map for the delocalization of one of the lone pairs on oxygen for the  $PCO^-$  anion. It illustrates

nicely the formation of a  $\pi(CO)$  bond due to the interaction with a  $\pi^*(CP)$  NBO.

Unfortunately, no simple correlation can be found between PC bond orders and PC stretching frequencies. This is certainly due to the effect, that the energy of the PC stretching mode not only depends on the covalent bond order but also on the ionic contribution as well as on the masses of the involved fragments. The extend of coupling between  $\nu(PC)$  and  $\nu(CX)$  which in some cases should rather be described as  $\nu_s$  and  $\nu_{as}$  of the  $PCX$  moiety must also be taken into account.

Figure 5 shows the experimental and the calculated  $^{31}P$  NMR chemical shifts at the MP2 level plotted against the s population at phosphorus (Table 6). As expected there is a good correlation. Again, it is obvious that the experimental  $\delta(^{31}P)$  values of  $PCOH$ , and even more so for  $PCF$ , do not fit into that scheme. Furthermore, the chemical shift of  $PCH$  cannot be explained by looking at the s electron density at the phosphorus atom alone. An explanation of this puzzling effect has not yet been found.

## Conclusions

The NMR chemical shifts and vibrational frequencies calculated for our series of  $\lambda^3$ -phosphaalkynes  $P\equiv C-R$  are in good agreement with experimentally obtained data. Notably the CCSD(T) values for the PC stretching frequency match within a few wavenumbers the parameters gained through spectroscopic

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methods, without the values being multiplied with an additional scaling factor. There is also a good quantitative agreement with the measured IR intensities at MP2 level. The calculated CCSD-(T) results show that the experimental PC stretching frequency for PCOLi lies between the two extreme cases,  $\text{PCO}^-$  and  $\text{PCOLi}$ . A similar observation can be seen for the  $^{31}\text{P}$  chemical shifts of PCOLi and PCSLi, for which the measured values are between the two extreme cases of the completely dissociated  $\text{PCX}^-$  anion and the lithiated species  $\text{PCXLi}$  ( $X = \text{O}, \text{S}$ ). These observations suggest some interaction of the lithium cation on one side and the  $\text{PCO}^-$  or  $\text{PCS}^-$  anions on the other side. As can be seen from Figure 3,  $f$  functions are important for the calculated  $\delta(^{13}\text{C})$  and  $\delta(^{31}\text{P})$  values but not as relevant as electron correlation. This suggests that methods of an even higher theoretical level are likely to yield even better results. When the resonance structures of PCR systems are discussed,

most species are best described as  $\lambda^3$ -phosphaalkynes. However, the cumulene-type structure **B** does play an important role especially when discussing the bonding situation of the anionic  $\text{PCS}^-$  and even more so for  $\text{PCO}^-$ . The phosphorus NPA charge is significantly more negative in  $\text{PCO}^-$  compared to  $\text{PCS}^-$  indicating larger  $\pi$  donation by the oxygen atom and thus a shift from resonance structure **A** to **B**.

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