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Reactivity of 1-Hydro-5-carbaphosphatrane Based on Tautomerization between Pentavalent Phosphorane and Trivalent Cyclic Phosphonite

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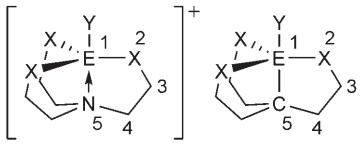
Abstract: The reaction behavior of 1-hydro-5-carbaphosphatrane (**1a**) was examined. Treatment of **1a** with oxidants such as 3-chloroperoxybenzoic acid (*m*CPBA) and *t*BuOCl gave cyclic phosphonate **2** and 1-chloro-5-carbaphosphatrane (**4**), respectively, via cyclic phosphonite **3**, a tautomer of **1a**. Compound **4** was readily hydrolyzed to afford **2**. Compound **1a** was also sulfurized via **3** by elemental sulfur to afford cyclic thioxophosphonate **5**, which was also obtained by reactions in the presence of bases. Treatment of **1a** with bases also proceeded through **3** to give an equilibrium mixture of the corresponding phenoxide anion **10** and the phosphoranide anion **9**, which was quenched with MeI to afford a mixture of **11** and 1-methyl-5-carbaphosphatrane (**1b**). Such reactivities are typical for neutral phosphoranes. Theoretical investigations of these reactivities were also performed.

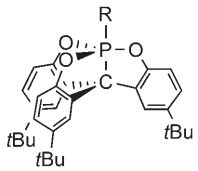
Keywords: ab initio calculations · carbaphosphatranes · phosphonite · tautomerism · tetradentate ligands

Introduction

There have been extensive studies on a wide variety of main group atranes, generally depicted as **A**.[1,2] Verkade and coworkers have investigated phosphorus-centered atranes, or phosphatranes (E = P), and have shown that they have unique structures, physical properties, and reactivities.[1a] Pro-phosphatranes—that is, the conjugated bases of phosphatranes—are known to be very strong neutral bases and have been utilized as catalysts in organic synthesis.[3] These unique features of phosphatranes are believed to be caused by the N→P dative bond. From such a viewpoint, it is particularly intriguing to consider how their properties will change when the N→P dative bond is replaced by a covalent bond with group 14 elements such as carbon (**B**).



A **B**



1a: R=H
1b: R=CH_3

We have recently reported the synthesis of the first carbon analogues of phosphatrane: the 5-carbaphosphatranes **1a** and **1b**.[4] It was revealed that 5-carbaphosphatranes have structural properties similar to those of the reported phosphatranes, since they have isoelectronic structures, while their transannular bonds are about three times stronger than those of silatranes.[4b] On the other hand, the

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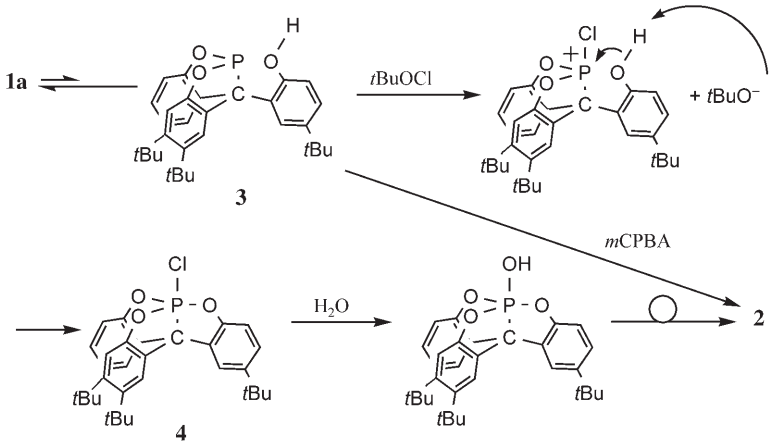
reactivities of 5-carbaphosphatranes would be expected to be different from those of phosphatranes, reflecting the differences in their bonding properties. Such comparisons between 5-carbaphosphatranes and phosphatranes should give important information about the relationship between bonding properties and reactivities of hypervalent compounds.

The 5-carbaphosphatrane **1a** can also be regarded as an alkoxy-substituted neutral hydrophosphorane, and one of the unique features of neutral hydrophosphoranes is known to be tautomerization between the pentavalent and trivalent species.[5] Here we report on the reactivity of 5-carbaphosphatrane **1a** based on tautomerization between pentavalent phosphorane and trivalent cyclic phosphonite, as elucidated both from experimental data and by theoretical calculations. Parts of this work have already been communicated.[4a]

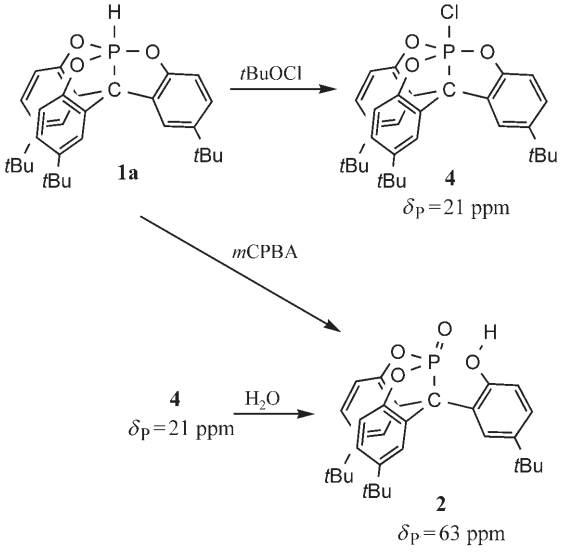
phorus atom of the tricoordinate phosphonite **3**, which is a tautomer of **1a** (Scheme 2). Such tautomerization has been reported for neutral hydrophosphoranes.[5] A phosphonite in the 6-carbaphosphatrane system, analogous to the phosphonite **3** proposed here as an intermediate, has recently been isolated and structurally characterized.[6]



Scheme 2.

Results and Discussion

Oxidation: A solution of 5-carbaphosphatrane **1a** and 3-chloroperoxybenzoic acid (*m*CPBA) in $CDCl_3$ was allowed to stand at room temperature, and the reaction was monitored by ^1H and ^{31}P NMR spectroscopy. Cyclic phosphonate **2**, showing a ^{31}P NMR signal at $\delta_P = 63$ ppm, was formed immediately (Scheme 1). Since there is no radical source under these reaction conditions, the cyclic phosphonate **2** is considered to be formed by oxidation at the central phosphorus atom of the tricoordinate phosphonite **3**, which is a tautomer of **1a** (Scheme 2). Such tautomerization has been reported for neutral hydrophosphoranes.[5] A phosphonite in the 6-carbaphosphatrane system, analogous to the phosphonite **3** proposed here as an intermediate, has recently been isolated and structurally characterized.[6]

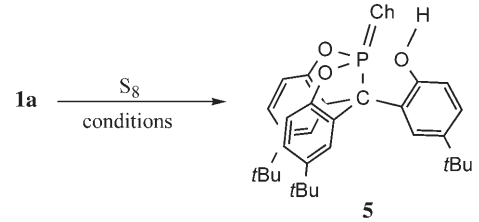


Scheme 1.

The 5-carbaphosphatrane **1a** was also easily oxidized by *t*BuOCl. In the case of *t*BuOCl, however, the reaction gave a new intermediate, the 1-chloro-5-carbaphosphatrane (**4**; Scheme 1), which showed a signal at $\delta_P = 21$ ppm in the ^{31}P NMR spectrum. The ^1H NMR spectrum of this intermediate showed a signal pattern corresponding to C_3 symmetry and a low-field shift of the aromatic protons *ortho* to the central carbon. The formation of **4** can also be explained by oxidation of the tautomer **3** by chlorine cation (Scheme 2). Unfortunately the isolation of the intermediate **4** was unsuccessful because **4** was readily hydrolyzed to the cyclic phosphonate **2** by atmospheric moisture. The cyclic phosphonite **3** was not observed in any spectroscopic measurement of **1a**, and no significant change was observed in the variable-temperature ^1H NMR spectra of **1a** over the range from −80 to 80 °C. These observations are reasonable, however, if the tautomer **1a** is—as predicted by theoretical calculations (vide infra)—thermodynamically much more favorable than **3**.

Sulfurization: The existence of tautomerization between **1a** and **3** was strongly supported by direct sulfurization of **1a**. Treatment of **1a** with elemental sulfur was investigated, and the results are summarized in Table 1. The reaction gave high yields of cyclic thioxophosphonate **5** (Scheme 3), which was considered to be formed through irreversible sulfurization of the tautomer **3**. However, the sulfurization needs higher reaction temperatures and longer reaction times than oxidations with *m*CPBA and *t*BuOCl, probably because the sulfurization was performed under neutral conditions while the oxidation reactions were carried out in the presence of proton sources such as benzoic acid or *t*BuOH. It is likely

Table 1. Sulfurization of 1-hydro-5-carbaphosphatrane (**1a**).



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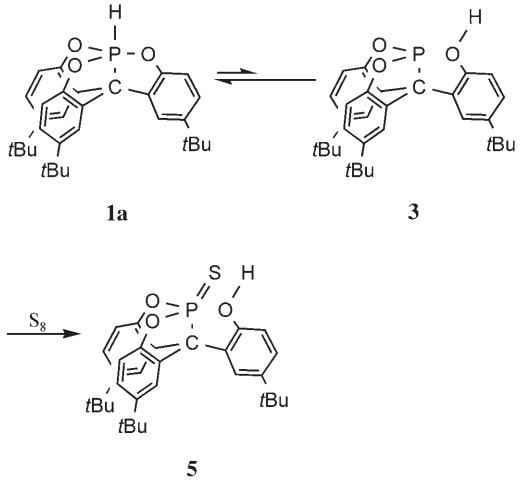
Conditions			Results
solvent	temp. [°C]	time	yield [%]
$CDCl_3$	80	2 days	0
$[D_8]$toluene	140	6 days	100
$[D_{10}]$xylene	160	16.5 h	100
$[D_8]$toluene[a]	140	2 days	100

[a] In the presence of 3.8 equivalents of benzoic acid.

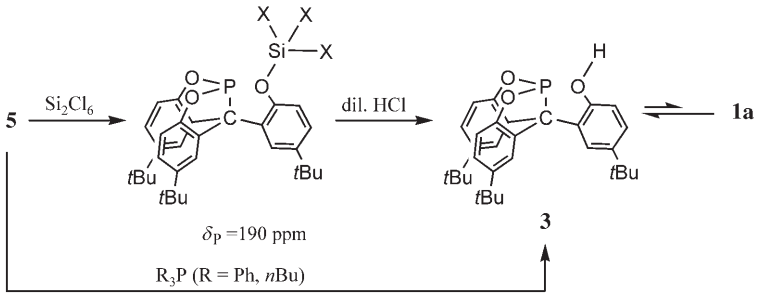


Scheme 3.

that these proton sources lower the barrier of the tautomerization between **1a** and **3**, as predicted by theoretical calculations (vide infra). These assumptions were verified by sulfurization in the presence of 3.8 equivalents of benzoic acid. The reaction was then complete after two days at 140 °C, while it took six days at the same temperature in the absence of benzoic acid.

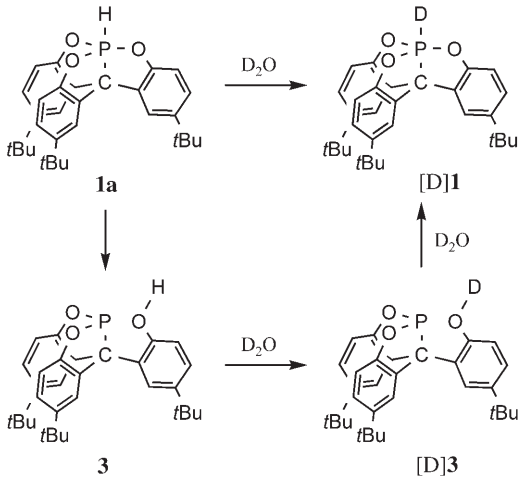
Desulfurization of thioxophosphonate 5: As mentioned above, cyclic phosphonite **3** was not observed experimentally when 5-carbaphosphatrane **1a** was used as a precursor. On the other hand, cyclic thioxophosphonate **5** was expected to be a good precursor of **3**, because phosphine sulfides are easily desulfurized by stronger trivalent phosphines or silicon reagents such as Si_2Cl_6.[7] Treatment of **5** with triphenylphosphine or tributylphosphine gave 5-carbaphosphatrane **1a** quantitatively (estimated by ^{1}H NMR spectroscopy). No intermediates such as cyclic phosphonite **3**, however, could be observed by ^{31}P NMR monitoring during the reaction. On the other hand, an intermediate giving a signal at $\delta_P = 190$ ppm was observed when **5** was treated with Si_2Cl_6 (Scheme 4). On quenching of the reaction with dilute hydrochloric acid, **1a** was obtained as the only product, although the isolated yield of **1a** was low (40 %) because of difficulty of separation from siloxane polymer. The results described in this section support the existence of the tautomerization from cyclic phosphonite **3** to 1-hydro-5-carbaphosphatrane (**1a**). Unfortunately, no unambiguous evidence of the existence of **3** could be obtained in the desulfurization by phosphines, due to the rapid tautomerization from **3** to **1a**. The silylated derivative of **3**, however, was observed at $\delta_P = 190$ ppm by ^{31}P NMR spectroscopy in the reaction with Si_2Cl_6, and the quantitative formation of **1a** by hydrolysis of the silylated compound also provides strong evidence for the tautomerization from **3** to **1a**.

H/D exchange: When the $CDCl_3$ solution of **1a** was allowed to stand for two months in the presence of D_2O (99.9 % atom D), H/D exchange of the P–H bond was observed and the final D content of [D]**1a** was 98 %. This reaction was significantly accelerated by acid; in the presence of DCl/D_2O it was complete within 15 h at room temperature. These H/D exchanges most probably proceed through tautomerization between 1-hydro-5-carbaphosphatrane (**1a**) and cyclic phosphonite **3** (Scheme 5), so these results are also consistent with the equilibrium between **1a** and **3**. The rates of H/D exchange under the pseudo-first order conditions were measured by ^{1}H NMR monitoring in $CDCl_3$ solution in the presence of AcOD (30.5–51.0 °C temperature range).



Scheme 4.

Eyring plot of the rates gave the activation parameters $\Delta H^{\neq} = 18.25$ kcal mol^{-1} and $\Delta S^{\neq} = -23.23$ cal mol^{-1} K^{-1}. Since H/D exchange of the phenolic hydroxy group would seem to be a fast process, it is likely that the rate-determining step is the tautomerization from the pentacoordinate carbaphosphatrane to the tricoordinate cyclic phosphonite, and that these activation parameters are those of the tautomerization. Although the $\Delta H^{\neq}$ value obtained here is smaller than the theoretically predicted value in the case of the water-cat-



Scheme 5.

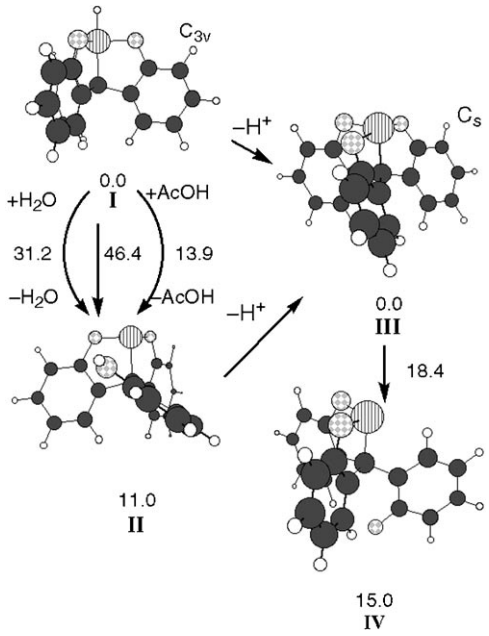


Figure 1. Potential energy surface for carbaphosphatrane. Neutral species are shown in the left column, while deprotonated anions are given on the right side. MP2/EXT//RHF/6–31G(d) enthalpy values are given in kcal mol^{-1}, including zero point energies from RHF/6–31G(d). Numbers next to arrows are the transition state energies. Only minimum-energy structures are illustrated, and possess no symmetry unless otherwise indicated. Transition state geometries are depicted in the Supplementary Material. The effect of solvent and *tert*-butyl substitution is not included, but is discussed in the text. The zero of energy for the ions is 344.3 kcal mol^{-1} above carbaphosphatrane. The structure of the pentacoordinated anion was obtained at the MP2/6–31G(d) level; see text.

alyzed system (31 kcal mol^{-1}), this difference could be attributable to the difference in acidity between water and acetic acid or the differences in the transition state structures, since the $\Delta H^{\neq}$ value decreased to 13.9 kcal mol^{-1} in the case of an acetic acid-catalyzed system (vide infra). The transition state of acetic acid-catalyzed tautomerism between **1a** and **3** has a seven-membered ring structure.

While such tautomerization between penta- and tricoordinate species has never been described for normal phosphatranes containing N→P dative bonds, it is not surprising that a neutral phosphorane **1a** with a covalent C–P bond should undergo such isomerization. In fact, as already noted above, we have recently been able to crystallize and determine the structure of the phosphonite tautomer in the 6-carbaphosphatrane system.[6] A reaction involving similar tautomerization has also been reported for an *o*-phosphinobenzoic acid.[8]

Theoretical calculations for the tautomerization of 1-hydro-5-carbaphosphatrane (1a) and its derivatives: Figure 1 shows the parent carbaphosphatrane system analyzed by theoretical calculations, in the absence of an additional chalcogen atom (O or S). Carbaphosphatrane **I** (a model of **1a**) is 11 kcal mol^{-1} more stable than the phenol isomer **II** (a model of the proposed tautomer **3**). The latter isomer can be reached via a transition state for [1,2] H-migration with a high barrier of 46 kcal mol^{-1}, or alternatively by transfer of a proton from a catalytic water molecule to oxygen, while at the same time a proton transfers from phosphorus to the water's oxygen. This type of transition state has angles similar to hydrogen bonds, so it has a lower barrier (31 kcal mol^{-1}) than the unimolecular proton migration.[9]

In the case of an acetic acid-catalyzed system, 5-carbaphosphatrane tautomerization occurs via a seven-membered transition state ($\Delta H^{\neq}$ = 13.9 kcal mol^{-1}), containing two reacting H-bonds (see Figure 2). H-bond adducts exist in both

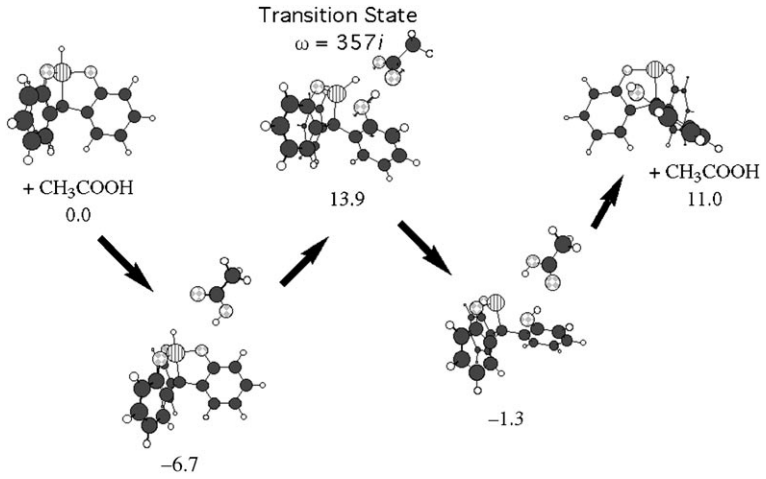


Figure 2. Calculated reaction pathway of acetic acid-catalyzed tautomerization. MP2/EXT//RHF/6–31G(d) enthalpy values are given in kcal mol^{-1}, including zero point energies from RHF/6–31G(d).

the entrance and exit channels of the tautomerization. The computed barrier (gas phase) of 13.9 kcal mol^{-1} is in good agreement with the observed (in solution) activation energy of 18.25 kcal mol^{-1}, reported in the preceding section.

Next, let us consider the oxidation and sulfurization of 1-hydro-5-carbaphosphatrane by theoretical calculations. However, Figures 3 and 4 begin with the unobserved neutral

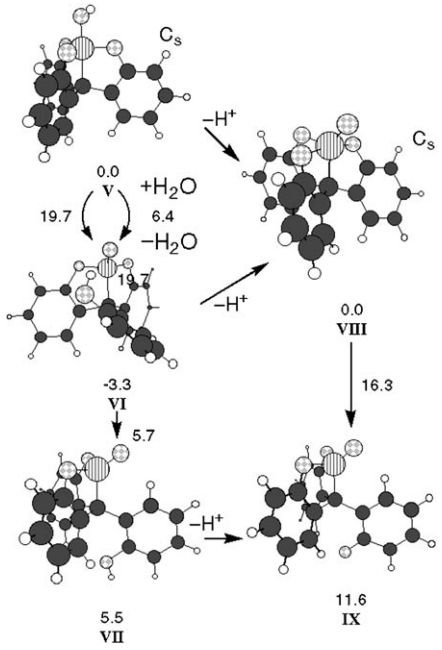


Figure 3. The potential energy surface for hydroxycarbaphosphatrane. See the caption of Figure 1 for further explanation. The zero of energy for ions is 329.5 kcal mol^{-1} above hydroxycarbaphosphatrane.

species hydroxycarbaphosphatrane **V** and mercaptocarbaphosphatrane **X**. Barriers for hydrogen migration are smaller, as the transition states for direct [1,2] H-migration are now four-membered rings rather than a three-membered ring. Proton transfers through catalytic water are even lower: just 6 or 10 kcal mol^{-1} for Ch = O or S. After migration of the hydrogen, the resulting tetracoordinate structures **VI** and **XI** have lower energies than the carbaphosphatranes **V** and **X**, respectively. This is presumably partially due to the potential for hydrogen bonding between the hydroxy group and the chalcogen atom of the P=X group, which cannot occur in the unchalcogenated system. An additional neutral isomer exists in both chalcogen systems, with the phenol ring rotated to position the hydroxy group at the bottom of the molecule (**VII** and **XII**). However, the barrier to rotation away from this isomer is very small. No 1-hydroxy or 1-mercapto derivatives were observed in the oxidation or sulfurization reactions of 1-hydro-5-carbaphosphatrane (**1a**), which is consistent with the calculated findings that the pentacoordinate carbaphosphatrane forms are less stable than the corresponding tetracoordinate phosphonate forms (Scheme 6).

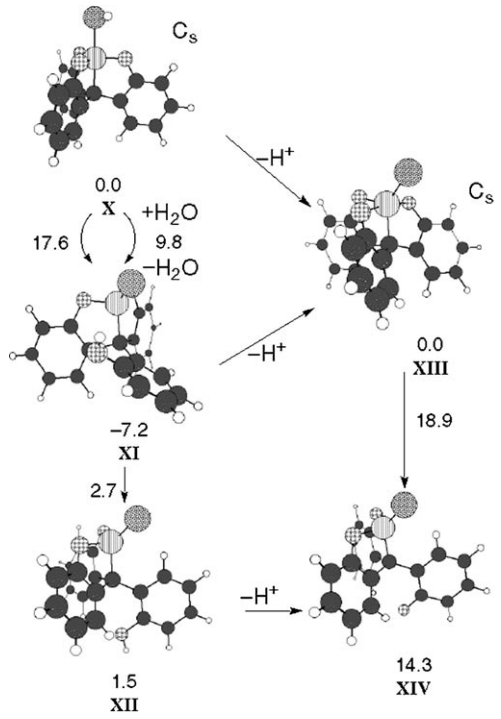
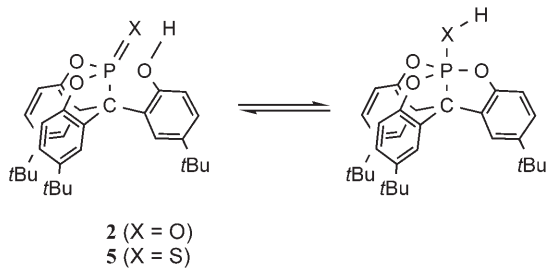


Figure 4. The potential energy surface for mercaptocarbaphosphatrane. See the caption of Figure 1 for further explanation. The zero of energy for ions is 322.5 kcal mol^{-1} above mercaptocarbaphosphatrane.

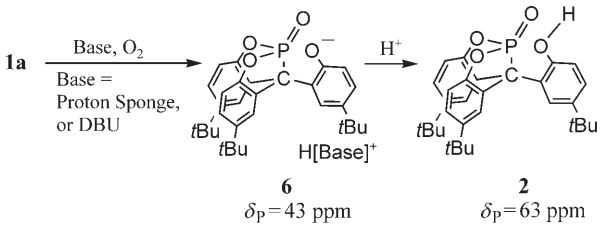


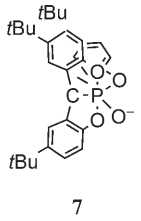
2 (X = O)
5 (X = S)

Scheme 6.

Reactions with bases: Although the parent phosphatranes (**A**; E = P, X = O, Y = H) are a kind of protonated phosphite, they are rather resistant to deprotonation by various bases. It has been reported that only *t*BuOK can abstract the protons of phosphatranes, while other well known strong bases such as proton sponge cannot deprotonate them.[10] Although 1-hydro-5-carbaphosphatrane (**1a**) has a structure and spectroscopic properties similar to those of previously reported phosphatranes, the reactivities of **1a** with bases would be expected to be different from those of phosphatranes because of its different bonding properties, as described before.[4b]

$CDCl_3$ solutions of **1a** were allowed to stand in the presence of bases such as proton sponge or DBU at room temperature in the open atmosphere. When the reaction was monitored by ^{31}P NMR, the signal (δ_P = 2.7 ppm) due to **1a** gradually changed to a signal at δ_P = 43 ppm (Scheme 7). It

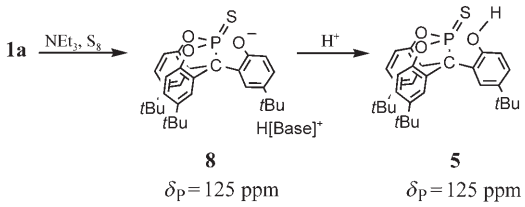




Scheme 7.

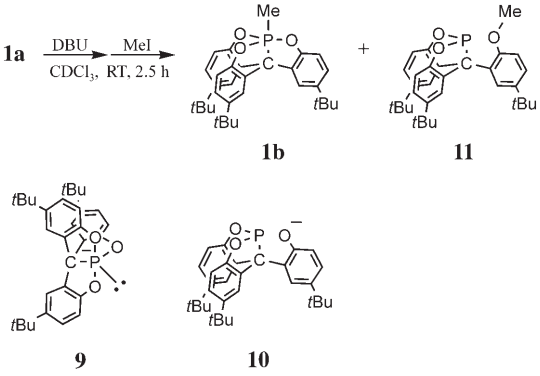
took a week to complete the reaction in the case of DBU and over two weeks in the case of proton sponge. When the product of these reactions was measured by ^{1}H NMR spectroscopy, three aromatic rings were observed in a ratio of 2:1, and no low-field shift of aromatic protons at the positions *ortho* to the central carbon was observed in this compound. These observations indicate that this compound does not maintain the carbaphosphatrane structure. When the compound was treated with hydrogen chloride, the cyclic phosphonate **2** was obtained, so the compound with the signal observed at $\delta_P = 43$ ppm could only be the phenolate anion **6** or its pentacoordinate tautomer **7**. The signal at $\delta_P = 43$ ppm is most likely to be attributable to **6** or an equilibrium mixture of **6** and **7**, in spite of the calculated energy order (Figure 3), since the signal due to the pentacoordinate species **7** should appear at much higher field.[11] The high-field shift by 20 ppm observed for **6** in relation to **2** is probably due to an equilibrium between **6** and **7**.

It was found that the proton of **1a** can be abstracted by amines, but the product was oxidized in the open atmosphere. When the same reaction was examined in a sealed tube, the reaction surprisingly did not proceed, although a small amount of anion **6** was formed in the early stage of the reaction, because of residual oxygen. These two experiments suggest that oxygen is necessary for progress of reactions between **1a** and amines to be observed. Treatment of **1a** with amine in the presence of sulfur instead of oxygen was also carried out, triethylamine being added to a $CDCl_3$ solution of **1a** in the presence of sulfur. When the reaction was monitored by ^{31}P NMR, the signal due to **1a** disappeared and a new signal was observed at $\delta_P = 125$ ppm (Scheme 8). Treatment of the reaction mixture with dilute hydrochloric acid afforded cyclic thioxophosphonate **5**, which coincidentally has the same ^{31}P chemical shift (but a different color and proton NMR). These results suggest that the initial signal observed at $\delta_P = 125$ ppm is due to the phenolate anion **8**, similarly to the reaction in the open atmosphere described above. However, in contrast to the reaction in the open atmosphere, no high-field shift was observed for **8** in relation to **5**.



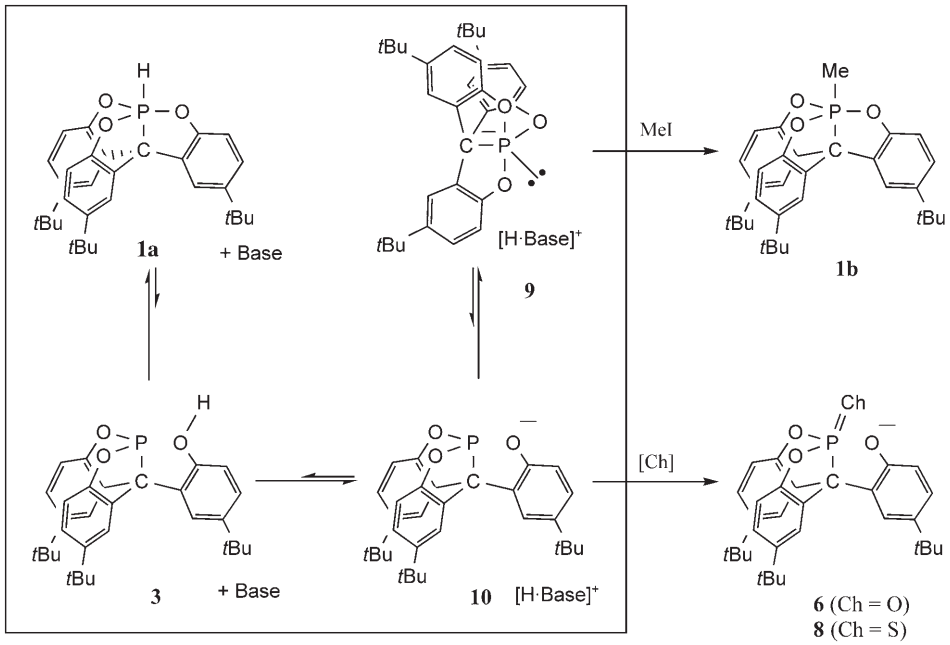
Scheme 8.

In the reactions between **1a** and amines, an anionic species should be generated, although none was observable. For this anion, there are two possible forms: one is the phosphoranide **9** and the other is the phenolate **10** (Scheme 9). It would be expected that anion **9** should give a 1-alkyl derivatives of **1a** on treatment with alkyl halide, so we examined the reaction between the anion of **1a**, generated by DBU, and methyl iodide. DBU was added to a fully degassed $CDCl_3$ solution of **1a**, and after addition of methyl iodide, the reaction mixture was allowed to stand at room temperature in a sealed tube (Scheme 9). The formation of the 1-methyl derivative **1b** was confirmed by ^{31}P NMR spectroscopy. This product is considered to be formed by the reaction between the phosphoranide **9** and methyl iodide. The signal due to cyclic phosphonite **11**, which is formed by the reaction between the phenolate **10** and methyl iodide, was also observed by ^{31}P NMR at $\delta_P = 190$ ppm.



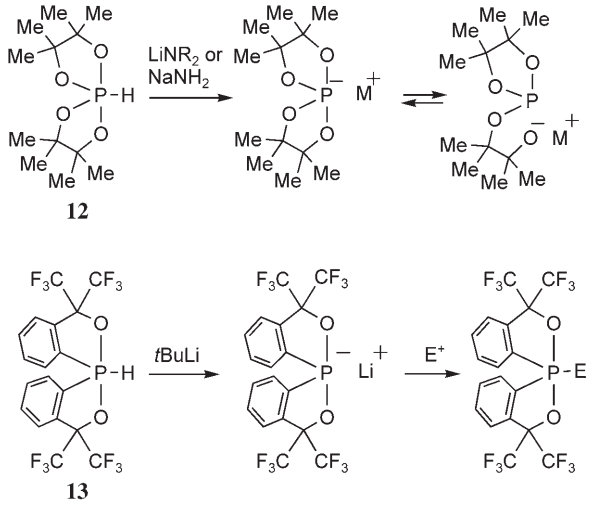
Scheme 9.

The possible mechanism for reactions between **1a** and amines is summarized in Scheme 10. The tautomer **3** is deprotonated by amine to give the ionic species **10**, which is irreversibly oxidized or sulfurized to give **6** or **8**, respectively. When the phosphoranide **9** reacts with methyl iodide, the 1-methyl derivative **1b** is formed. The species enclosed in a square in Scheme 10 are in equilibrium and only 5-carbaphosphatrane **1a** can be observed by NMR spectroscopy under the equilibrium conditions. The result that no change was observed on treatment of **1a** with amines in a sealed tube is consistent with such equilibrium.



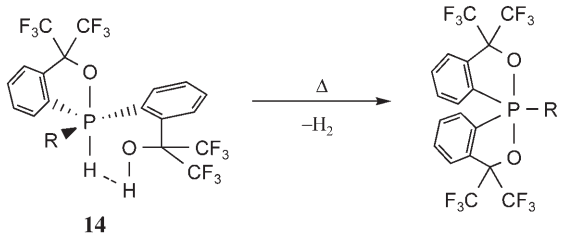
Scheme 10.

On the other hand, it was reported that phosphoranes **12** and **13**, in which a hydrogen atom is located at an equatorial position, are deprotonated directly by relatively strong bases such as $NaNH_2$, $LiNR_2$, and so on.[5d,12] In view of the nature of three-center, four-electron bonds, the apical P–H hydrogen atom of **1a** would be considered to have more hydridic character than the equatorial hydrogen atoms of **12** and **13** (Scheme 11). Indeed, the P–H hydrogen of phosphorane **14**,



Scheme 11.

which is located at the apical position, has been reported to act as a hydride and to react with an alcoholic proton to give rise to the intramolecular elimination of a hydrogen molecule (Scheme 12).[13] The deprotonation in the reaction



Scheme 12.

of **1a** with bases is therefore considered to have proceeded from tautomer **3**, it being taken into consideration that the bases used were much weaker than those used for the deprotonation of **12** and **13**.

Theoretical calculations on anionic species: Deprotonation of either the carbaphosphatrane **I** or the phenol isomer **II**, followed by geometry optimization, gives the same ionic structure: the pentacoordinate ion **III** shown in the upper right of Figure 1.[14] The ion **III** is described as pentacoordinate since its fifth coordination site is a P lone pair. This ion has an axial oxygen (O-P-O angle is 169.7°, PO distances are 1.930 Å) in order to place the P lone pair in an equatorial site, so as a result, the carbon is also equatorial. Rotation about one of the C–C bonds connecting to the C-5 atom gives an isomeric ion **IV**, shown at the bottom right of the figure, with a P-C-C-C torsion angle equal to 181.2°, with an energy 15 kcal mol^{-1} above that of the pentacoordinate ion **III**. The transition state separating this transoid ion **IV** from the more stable pentacoordinate ion **III** occurs at a P-C-C-C torsion angle of 126.0°, and lies 3.4 kcal mol^{-1} above it.

Before going on, Figures 1, 3, and 4 contain only the highest-level energy results. Some idea of the convergence of these results may be seen by comparing the zero-point corrected energy differences for RHF/6–31G(d), RHF/EXT, and MP2/EXT. For the protonated neutrals, the energy of the phenol structure **II** is 1.4, 5.9, and 11.0 kcal mol^{-1}, while the transoid ion **IV** lies 6.7, 4.7, and 13.6 kcal mol^{-1} above the corresponding pentacoordinate forms **I** and **III**, respectively, at these three levels.

Deprotonation of the chalcogenated carbaphosphatranes **V** and **X**[15] or their most stable tetracoordinate neutral isomers **VI** and **XIV**[16] gives the pentacoordinate anions **VIII** and **XIII** shown in the top right sides of Figures 3 and 4, re-

spectively. Both ions have axial oxygen atoms, with O–P–O angles of 168.0° and 168.4° and C–P–Ch angles of 137.8° and 137.1° for Ch = O and S respectively. Additional ionic isomers **IX** and **XIV** exist with the phenoxide oxygen rotated to the bottom of the molecule, and are 11.6 or 14.3 kcal mol^{-1} above the pentacoordinate ion for Ch = O and S. These transoid ions may be considered to arise from deprotonation of the corresponding transoid phenol structures. Relative to their neutral precursors, however, these ionic minima have larger barriers separating them from rotation into the more stable pentacoordinate ions: 4.7 and 4.6 kcal mol^{-1} for Ch = O or S, respectively. These rotational barriers are larger than the 3.4 kcal mol^{-1} barriers observed when no chalcogen is present, and should impart enough kinetic stability to these ions to allow them to be seen at room temperature, if they are produced.

There are three additional factors to consider in deciding whether the pentacoordinate ion is indeed more stable than the transoid ion. The first of these is that the ions are generated in chloroform solvent. Figures 1, 3, and 4 show large energy differences between neutrals and ions due to the use of a gas phase energy for the proton, but also due to omission of the stabilization of the anions by the solvent. Accordingly, PCM calculations at the RHF/EXT level were carried out on the anions in order to assess the effect of the $CHCl_3$ solvent, with a dielectic constant of 4.9. The dielectic continuum PCM model preferentially stabilizes the pentacoordinate ions, since these have a larger center of mass dipole moment than the transoid ions. For example, Ch = O has a dipole of 8.55 Debye for the pentacoordinate ion, but 6.35 for the transoid ion. The energy preference at the RHF/EXT level for the pentacoordinate ion is changed from the gas-phase value of −0.2 kcal mol^{-1} to 4.2 kcal mol^{-1} for Ch = O, and from 4.9 to 9.0 kcal mol^{-1} for Ch = S.

The second factor is the possible influence of the bulky *tert*-butyl groups, located at the carbons *para* to the hydroxy group. Inspection of the transoid ion in Figures 3 and 4 indicates there is room next to the chalcogen for the *tert*-butyl, and indeed this is so. RHF/6–31G(d) geometry optimization for both chalcogen systems with all three *tert*-butyl groups added gives similar pentacoordinate and transoid ion structures. MP2/EXT calculations are not possible with the large basis sets after these *tert*-butyl groups are added, so the RHF/EXT single-point energy of the transoid ion without *tert*-butyl is −0.2 kcal mol^{-1}, and with the *tert*-butyl groups present, −2.4 kcal mol^{-1}. For Ch = S, the situation is similar: the RHF/EXT relative energy of the transoid ion without the *tert*-butyl groups is 4.9 kcal mol^{-1}, while with them it is 2.9 kcal mol^{-1}. The effect of the *tert*-butyl groups is thus to stabilize the transoid ions by 2 kcal mol^{-1}.

A final assessment of the energy difference between the two ion conformations can now be made. Starting from the RHF/EXT energy difference, the following effects have been considered separately: zero point energy differences found with RHF/6–31G(d), electron correlation found with MP2/EXT, PCM solvent effects found with RHF/EXT, and finally the steric influence of *tert*-butyl groups found with RHF/EXT. If it is assumed that these various effects are additive, the energy of the Ch = O transoid ion relative to the pentacoordinate ion is predicted to be $-0.22-0.06+11.92+4.46-2.23 = 13.9$ kcal mol^{-1}. The analogous calculation for Ch = S is $4.87-0.31+9.75+4.08-1.98 = 16.4$ kcal mol^{-1}. Thus the calculations indicate that in all cases, including that in which no additional chalcogen is present, the most stable ions are pentacoordinate forms, with axial O–P–O bonds.

In contrast with these theoretical results, no pentacoordinate anions were observed experimentally. Theoretical calculations predicted that the pentacoordinate anions should be more stable than the tetracoordinate anions, but experimental results suggested the opposite results: that is, the tetracoordinate anions are more stable than the pentacoordinate ones. A third factor contributing to the difference between the gas-phase anion calculations and the experimental system is the presence of the counter cation (triethylammonium cation). Because the theoretical calculations were performed in the absence of any counter cation, stabilization effects due to interactions between the anions and the counter cation were not considered. As suggested by an anonymous referee, a counter cation would be expected to associate itself with the oxygen anion in the phenoxide, and thus provide some further stabilization to species such as **IV**, **IX**, and **XIV**.

Conclusion

Reactions of 1-hydro-5-carbaphosphatrane based on tautomerization to the trivalent cyclic phosphonite, not definitively observed by spectroscopic methods, have been studied experimentally and analyzed by theoretical calculations. The theoretical calculations found relative minima for all intermediates proposed here—namely **II**(**3**), **III**, **IV**, **VIII** (**7**), and **XIII**, as well as the observed species **I** (**1a**), **VI** (**2**), **IX** (**6**), **XI** (**5**), and **XIV** (**8**)—but in some cases disagree in terms of their relative stabilities, presumably because of the omission of the counter cation in the calculations. The existence of the key phosphonite intermediate **3** proposed here to explain many of the reactions is supported not only by the computations reported here, but also by our recent isolation of the analogous phosphonite in 6-carbaphosphatrane.[12] 1-Hydro-5-carbaphosphatrane was easily oxidized or sulfurized via tautomerized species, and treatment of the sulfurized derivative, cyclic thioxophosphonate, with trivalent phosphines regenerated 1-hydro-5-carbaphosphatrane. 1-Hydro-5-carbaphosphatrane was deprotonated by various amino bases and oxidized and sulfurized compounds were obtained, although the deprotonated species were not observed spectroscopically. These reactivities of 1-hydro-5-carbaphosphatrane are quite different from those of parent phosphatranes, reflecting the different bonding properties, but are typical for aryloxy-substituted pentacoordinate hydrophosphoranes. The long reaction times reported here for many of the reactions are indicative of a greater stability of

5-carbaphosphatranes than of other atranes, due to their strong transannular P–C bonds.

Experimental Section

General methods: Melting points were determined on a Yanaco micro melting point apparatus. All melting points were uncorrected. THF was purified by distillation from sodium diphenylketyl under argon before use. $CDCl_3$ was distilled from calcium hydride before use. [D_8]Toluene, [D_{10}]xylene, and [D_6]benzene were dried over sodium before use. High pressure liquid chromatography (HPLC) was performed by LC-918 with JAIGEL 1H+2H columns (Japan Analytical Industry) with chloroform as solvent. The ^{1}H NMR (500 and 270 MHz) and ^{13}C NMR (126 MHz) spectra were measured in $CDCl_3$, [D_8]toluene, [D_{10}]xylene, or [D_6]benzene with a Bruker DRX 500 spectrometer and a JEOL EXcalibur270 spectrometer with tetramethylsilane or residual peaks of deuterated solvents as an internal standard. The ^{31}P NMR (109 MHz) spectra were taken in $CDCl_3$, [D_8]toluene, [D_{10}]xylene, or [D_6]benzene with a JEOL EXcalibur270 spectrometer, with 85% H_3PO_4 as an external standard. Mass spectra were recorded with a JEOL JMX-SX102 mass spectrometer.

H/D exchange experiment with 1-hydro-5-carbaphosphatrane (1a) and DCl: DCl/D_2O (0.1 mL) was added to a solution of **1a** (12.8 mg, 0.0248 mmol) in $CDCl_3$ (0.5 mL). The reaction mixture was allowed to stand at room temperature and monitored by ^{1}H and ^{31}P NMR. The H/D exchange was complete within 15 h at room temperature. [D]**1a**: ^{31}P NMR (109 MHz, $CDCl_3$): δ = 2.3 ppm (t, ^1J(P,D) = 130 Hz).

Kinetic measurement of H/D exchange for 1-hydro-5-carbaphosphatrane (1a) with AcOD: A $CDCl_3$ (0.5 mL) solution of **1a** (ca. 10 mg) and AcOD (0.05 mL) were placed in a 5 mm ∅ NMR tube. After several freeze-pump-thaw cycles, the tube was evacuated and sealed. The solution was heated at each temperature (30.5, 36.2, 40.7, 45.2, 51.0 °C) in a thermostat. The rate of H/D exchange was obtained by measuring the decrease of the amount of **1a** by ^{1}H NMR spectroscopy. At each temperature, the data gave a good first-order plot and rate constants were calculated from these data. The Eyring plot of the rate constants gave activation parameters ($\Delta H^{\neq}$ = 18.25 kcal mol^{-1} and $\Delta S^{\neq}$ = −23.23 cal mol^{-1} K^{-1}).

Oxidation reaction with 1a and *m*CPBA: $CDCl_3$ (0.5 mL) was added under argon to a mixture of **1a** (38.3 mg, 0.0783 mmol) and *m*CPBA (36.4 mg, 0.148 mmol). The mixture was allowed to stand at room temperature for 15 h, treated with aq. $NaHCO_3$, and extracted with $CHCl_3$. The extracts were dried over anhydrous $MgSO_4$. After removal of the solvent, the crude reaction products were separated by HPLC to give a mixture of **2** and an unidentified product (δ_P = −18 ppm) (10.7 mg).

Oxidation reaction with 1a and *t*BuOCl: *t*BuOCl (20 μL, 0.18 mmol) was added under argon to a solution of **1a** (43.0 mg, 0.0880 mmol) in $CDCl_3$ (0.5 mL) and the mixture was allowed to stand at room temperature for 2 days. After removal of the solvent, the residue was subjected to HPLC to give cyclic phosphonate **2** (25.6 mg, 58%). Compound **2**: colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C): δ = 1.24 (s, 9H), 1.25 (s, 18H), 6.69 (d, J = 8.6 Hz, 1H), 6.97 (d, J = 8.6 Hz, 2H), 7.07 (dt, J = 8.4, 2.2 Hz, 1H), 7.19–7.29 ppm (m, 5H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 27 °C): δ = 31.4 (s), 31.6 (s), 34.2 (s), 34.6 (s), 47.8 (d, J(P,C) = 105 Hz), 112.9 (d, J(P,C) = 12.4 Hz), 116.3 (s), 119.2 (s), 123.2 (d, J(P,C) = 15.8 Hz), 125.3 (s), 125.5 (s), 126.5 (s), 130.9 (d, J(P,C) = 8.0 Hz), 141.6 (s), 147.2 (s), 149.6 (d, J(P,C) = 12.3 Hz), 153.1 ppm (s); ^{31}P NMR (109 MHz, $CDCl_3$, 27 °C): δ = 63 ppm; HRMS (70 eV) *m/z* calcd for $C_{31}H_{37}O_4P$ 504.2429; found 504.2436.

Reaction between 1a and elemental sulfur: [D_{10}]xylene (0.5 mL) was added to a mixture of **1a** (21.1 mg, 0.0432 mmol) and elemental sulfur (20.2 mg, 0.0629 mmol) in a 5 mm ∅ Pyrex glass tube. After several freeze-pump-thaw cycles, the tube was evacuated and sealed and the solution was heated at 160 °C for 16.5 h. After removal of the solvent under reduced pressure, the crude reaction products were separated by HPLC to afford cyclic thioxophosphonate **5** (23.1 mg, quant.). Compound **5**: colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$, TMS, 27 °C): δ = 1.23 (s, 9H), 1.25 (s, 18H), 5.21 (s, 1H), 6.84 (d, J = 8.4 Hz, 1H), 6.96 (d, J = 8.4 Hz, 2H), 7.19–7.29 (m, 4H), 7.33 ppm (brs, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 27 °C): δ = 31.4 (s), 31.5 (s), 34.2 (s), 34.6 (s), 57.6 (d, J(P,C) = 74 Hz), 113.0 (d, J(P,C) = 8.4 Hz), 117.7 (d, J(P,C) = 3.3 Hz), 121.8 (d, J-(P,C) = 2.5 Hz), 123.1 (s), 125.7 (s), 126.7 (d, J(P,C) = 3.6 Hz), 127.0 (d, J(P,C) = 6.9 Hz), 131.1 (s), 143.4 (d, J(P,C) = 2.4 Hz), 147.4 (s), 151.6 (d, J(P,C) = 5.0 Hz), 152.3 ppm (d, J(P,C) = 4.9 Hz); ^{31}P NMR (109 MHz, $CDCl_3$, 27 °C): δ = 125 ppm; HRMS (70 eV): *m/z* calcd for $C_{31}H_{37}O_3PS$ 520.2201; found 520.2195.

Desulfurization reaction with 5 and triphenylphosphine: $CDCl_3$ (0.5 mL) was added to a mixture of **5** (19.5 mg, 37.5 μmol) and triphenylphosphine (39.3 mg, 0.150 mmol) in a 5 mm ∅ Pyrex glass tube. After several freeze-pump-thaw cycles, the tube was evacuated and sealed. The solution was heated at 85 °C for 1 month with monitoring by ^{1}H and ^{31}P NMR. The conversion yield of **1a** was estimated to be 65% by ^{1}H NMR spectroscopy.

Reactions between 1a and bases in open atmosphere: DBU (0.030 mL, 0.20 mmol) was added to a solution of **1a** (20.6 mg, 0.0422 mmol) in $CDCl_3$ (0.5 mL). The mixture was allowed to stand in open atmosphere at room temperature for 7 d, treated with hydrochloric acid, and extracted with $CHCl_3$. The extracts were dried over anhydrous $MgSO_4$. After removal of the solvent, the crude reaction products were separated by HPLC to give cyclic phosphonate **2** (6.6 mg, 31%, conv. 41%).

Reaction between 1a and triethylamine in the presence of elemental sulfur: Triethylamine (0.10 mL, 0.72 mmol) was added to a mixture of **1a** (101.2 mg, 0.207 mmol) and elemental sulfur (65.4 mg, 2.04 mmol) in $CDCl_3$ (0.5 mL). The solution was allowed to stand at room temperature for 3 d. The mixture was treated with hydrochloric acid and extracted with $CHCl_3$, and the extracts were dried over anhydrous $MgSO_4$. After removal of the solvent, the crude reaction products were separated by HPLC to give cyclic thioxophosphonate **5** (78.3 mg, 78%).

Reaction between 1a and DBU followed by treatment with iodomethane: A solution of **1a** (41.8 mg, 0.0855 mmol) in $CDCl_3$ (0.5 mL) was degassed by six freeze-pump-thaw cycles and DBU (0.10 mL, 0.67 mmol) was then added. After the mixture had been allowed to stand at room temperature for 1 h, iodomethane (0.03 mL, 0.48 mmol) was added. After several freeze-pump-thaw cycles, the tube was evacuated and sealed. The mixture was allowed to stand at room temperature for 3 d and the reaction was monitored by ^{31}P NMR spectroscopy. The new signal attributable to cyclic phosphonite **12** was observed at δ = 190 ppm with a signal for 1-methyl-5-carbaphosphatrane **1b** at δ = 21 ppm. The mixture was treated with hydrochloric acid and extracted with $CHCl_3$, and the extracts were dried over anhydrous $MgSO_4$. After removal of the solvent, the crude reaction products were separated by HPLC to give **1b** (26.4 mg, 62%). Product **12** or its derivative was not obtained.

Calculation methods: Calculations were performed with closed shell SCF (RHF)[17] and second order Moller–Plesset perturbation theory (MP2)[18] methods. On the basis of our earlier finding[4b] that RHF and MP2 structures for carbaphosphatrane are quite similar, all structures were obtained at the RHF/6–31G(d) level.[19] To obtain more reliable energy values, MP2 calculations were performed with these structures with an extended triple zeta basis set. This basis has additional polarization functions for the hypervalent P (3df), and diffuse functions are added to this atom and all H, C, O, S atoms adjacent to it, as these are more electronegative and several anions are considered, and finally H atom polarization is added, which is important in reactions involving proton transfers. The quality of this basis can be described as 6–311++G(3df,d,p), except for the C_6H_4 benzene rings, where just the 6–31G(d) basis was used to keep the computations tractable. This extended basis set is referred to here as EXT.[20] Zero point energy corrections from RHF/6–31G(d) are added to MP2/EXT energies to obtain the reported zero degree enthalpies. It is generally true that the basis set extensions shifts the energy by a few kcal mol^{-1}, not always in the same directions, while MP2 always preferentially stabilizes pentacoordinate forms, by 7–12 kcal mol^{-1} in ions, and smaller amounts in the neutral molecules. Solvent effects were modeled with the Integral Equation Formalism implementation of the Polarizable Continuum Model.[21] All calculations used Cartesian Gaussians

rather than spherical harmonics, and were carried out with the GAMESS program package.[22]

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[15] At the RHF/6–31G(d) level used for structure determinations, the HCh-carbaphosphatranes deprotonate to C_3 symmetry molecules, with linear C-P-Ch angles. These lie 12.0 and 14.3 kcal mol^{-1} above the pentacoordinate isomers shown, for Ch = O and S respectively. Both have 0.1 kcal mol^{-1} barriers for pseudorotation to the pentacoordinate ion with axial oxygens. MP2/EXT single-point calculations at these pseudorotation transition states show lower energy than for the C_3 minima, so these minima are omitted from Figures 3 and 4 as being probably nonexistent isomers.

[16] For the case of Ch = O only, at the RHF/6–31G(d) level used for structure determinations, deprotonation of the more stable phenol isomer gives a shallow minimum, with a PCCC torsion angle = 52.1°. Its structure is almost unchanged from the neutral parent's geometry, apart from the proton being absent. This minimum lies 3.1 kcal mol^{-1} above the pentacoordinate ion, and is separated from it by a barrier of just 0.2 kcal mol^{-1}. Since MP2/EXT single-point calculations on this transition state lie below the energy of this tetracoordinate ion, this minimum is omitted from Figure 3 as being probably nonexistent. Ch = S shows no such minimum, as removal of the proton from the phenol parent's structure followed by geometry optimization leads directly to the pentacoordinate ion.

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