Figure 2. Kinetic absorption changes of phytochrome at 660 (a) and 690 nm (b). ● and — indicate experimental results and fitting curves, respectively. The kinetics is mainly probing the recovery of the ground-state depletion (660 nm) and the appearance of the primary product (690 nm), both of which are well fit by a single exponential with the same time constant of 24 ps. It is noted that this time constant (24 ps) is obtained throughout the entire 650–720 nm wavelength region, indicating that all primary processes including decay of Pr*, recovery to original Pr, and appearance of the primary product can be described by a single kinetic component.

through a microcell at 2 °C (2-mm light path) and irradiated with far-red light during experiments to convert the Pfr produced back to the Pr form. The λ_{max} of the sample is located at 666 nm, and the absorbance at λ_{max} is 0.59 in a 2-mm path length. The specific absorption ratio (A_{666nm}/A_{280nm}) is 0.98. The present experiments are carried out under the low excitation conditions (12% of molecules are excited), in which the absorption decrease is proportional to the excitation energy.

Upon excitation of the Pr form of the phytochrome sample with a sub-picosecond pulse (600 nm, 0.8 ps), we observed rapid depletion of the original absorption in the 650–740 nm wavelength region (Figure 1, at 3 ps). The spectral differences between the transient absorption at 3 ps and the original absorption (broken line) imply that the transient spectrum contains an excited-state absorption (mainly <670 nm) and a stimulated emission (mainly >670 nm). In other words, the excited phytochrome molecule is still in its excited state (Pr*) at 3 ps. The depletion signal recovers, accompanied by the appearance of the product absorption of positive signal at 675–730 nm. Kinetic changes at 660 (mainly probing ground-state recovery) and 690 nm (probing product rise as well as ground-state recovery) yield the same time constant of 24 ± 2 ps (see Figure 2), indicating that the rise time of the product is 24 ps as are the lifetime of Pr* and ground-state recovery time. Thus, the primary reaction rate of the present phytochrome sample is determined to be $(24 \text{ ps})^{-1}$.

Time-resolved fluorescence measurements on a sample with same preparation (114-kDa pea phytochrome in buffer) previously determined the lifetime of Pr* to be 34 ps, which was the predominant component (97%) among three.[4e] The difference of the lifetimes may be due to time resolution of the apparatuses (0.8 ps for the current study vs 40 ps for the previous study). In the fluorescence studies, intact phytochrome displayed a slightly larger lifetime of Pr* (39 ps for 121-kDa pea phytochrome),[4e] suggesting that the native chromophore may possess a longer lifetime. Our present observation is considerably different from the previous picosecond absorption study, in which the negative transient absorption at 665 nm increases in the first 25 ps and decays to zero by 50 ps (ref 3). The difference is unclear, as the present results clearly show instantaneous bleaching and recovery in 24 ps at 660 nm that coincide with the product formation time (Figure 2).

The spectral change is complete in approximately 100 ps (Figure 1). The difference spectrum is similar to that between Pr and lumi-R, which has been reported to be the primary intermediate.[9] The detailed spectral analysis will be given elsewhere.[10] Although there is no direct proof of the structures of the intermediates, generation of the primary product should be due to the confor-

mational change of the chromophore, probably photoisomerization from the 15-Z to 15-E form.[11] It should be noted that isomerization of rhodopsins, such as rhodopsin,[5d] bacteriorhodopsin,[5a–c] and halorhodopsin,[5e] takes place in the sub-picosecond regime. In these molecules, the reaction time (200 fs for rhodopsin[5d]) indicates that an essentially barrierless transition is realized in formation of the product and effective competition with fast intramolecular relaxation. It is generally accepted that fast reaction results in highly efficient photoisomerization ($\phi = 0.67$ for rhodopsin). In contrast, our results suggest that the photoisomerization of phytochrome is 2 orders of magnitude slower than that of rhodopsins. It is interesting to compare the rate with that of rhodopsins. The rate presently obtained is "slow", whereas the efficiency of the functional photoreaction (Pr → Pfr) is never low. The quantum yield has been reported to be 0.5 or higher.[12] Thus the present work indicates a greater variety of mechanisms of photoreceptive pigments in nature.

Finally, the present transient absorption study has provided the primary reaction rate for phytochrome, which will help lead to an understanding of its reaction mechanism. It has also opened the question of how the system can control its efficient primary reaction even with a slow rate constant.

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Synthesis and X-ray Crystal Structure of [(i-Pr₂N)₂P(H)CP(N-i-Pr₂)₂]⁺CF₃SO₃⁻: A Carbene, a Cumulene, or a Phosphaacetylene?

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The recent isolation of stable (phosphanyl)(silyl)carbenes $(R_2PCSiMe_3)$[1] has prompted considerable discussion of the best description of their ground states[2] (Scheme I). Calculations[3] led to the conclusion that they were best formulated as multiply bonded λ^5-phosphaacetylenes **B** or phosphorus vinyl ylides **C**,

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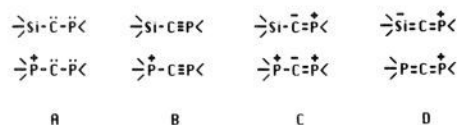(2) (a) Dagani, R. *Chem. Eng. News* **1991**, *69* (4), 19. (b) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 674.
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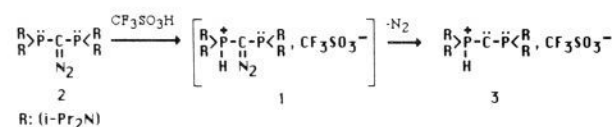
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Scheme I

$$\overset{..}{\underset{}{\rightarrow}Si\text{-}\overset{..}{C}\text{-}\overset{..}{P}<} \qquad \rightarrow Si\text{-}C\equiv P< \qquad \overset{-}{\rightarrow}Si\text{-}\overset{..}{C}\overset{+}{=}P< \qquad \overset{-}{\rightarrow}Si=C\overset{+}{=}P<$$

$$\overset{..}{\underset{}{\rightarrow}\overset{..}{P}\text{-}\overset{..}{C}\text{-}\overset{..}{P}<} \qquad \rightarrow\overset{+}{P}\text{-}C\equiv P< \qquad \overset{+}{\rightarrow}\overset{+}{P}\text{-}\overset{-}{C}\overset{+}{=}P< \qquad \rightarrow P=C\overset{+}{=}P<$$

A   B   C   D

Scheme II

$$\underset{\underset{2}{\overset{|}{N_2}}}{\overset{R}{\underset{R}{>}}}\overset{..}{P}\text{-}\overset{..}{C}\text{-}\overset{R}{\underset{R}{<}} \xrightarrow{CF_3SO_3H} \left[\underset{\underset{H}{\overset{|}{N_2}}}{\overset{R}{\underset{R}{>}}}\overset{+}{P}\text{-}\overset{..}{C}\overset{R}{\underset{R}{<}}, CF_3SO_3^- \right] \xrightarrow{-N_2} \underset{\overset{|}{H}}{\overset{R}{\underset{R}{>}}}\overset{+}{P}\text{-}\overset{..}{C}\text{-}\overset{..}{P}\overset{R}{\underset{R}{<}}, CF_3SO_3^-$$

R: (i-Pr_2N)   1   3

Figure 1. Ball and stick view of **3**. Selected bond distances (Å) and angles (deg): P(1)–N(1), 1.635 (4); P(1)–N(2), 1.641 (4); P(1A)–N(1), 1.622 (5); P(1A)–N(2), 1.638 (5); P(1)–C(2), 1.605 (5); P(1A)–C(2), 1.616 (5); P(2)–C(2), 1.548 (4); P(2)–N(3), 1.632 (3); P(2)–N(4), 1.635 (3); P(1)–C(2)–P(2), 165.1 (4); P(1A)–C(2)–P(2), 164.1 (4); C(2)–P-(2)–N(3), 126.3 (2); C(2)–P(2)–N(4), 126.7 (2); N(3)–P(2)–N(4), 107.0 (2). The minor parts of the disordered cation are shown by dotted atoms.

although they featured both carbene and phosphorus–carbon multiple bond reactivity.[1] The absence of a crystal structure analysis[4] precludes a definitive answer. So far, attempts to prepare stable phosphanylcarbenes bearing other than silyl groups at the carbene center have failed.[5] Since silyl and phosphonio groups are isoelectronic and isovalent, it was of interest to prepare a (phosphanyl)(phosphonio)carbene which can also be described by four different structures A–D (Scheme I). Here we report the synthesis, X-ray crystal structure, and equilibrium geometry obtained on the self-consistent-field (SCF) level of the [bis(di-isopropylamino)phosphanyl][bis(diisopropylamino)hydrogeno-phosphonio]carbene (**3**).

We chose to prepare, as a precursor, the corresponding diazo compound **1** by protonation of bis[bis(diisopropylamino)phos-phanyl]diazomethane (**2**).[6] When a dichloromethane solution of **2** was treated with a stoichiometric amount of trifluoro-methanesulfonic acid at –40 °C, a clean reaction occurred, leading not to the expected diazo compound **2** but directly to the desired "(phosphanyl)(phosphonio)carbene" **3** (Scheme II).

Derivative **3** was obtained as extremely air sensitive yellow crystals (mp 88 °C dec; 76% yield).[7] The ^{31}P NMR spectrum showed two doublet of doublet of quintets at +3.14 (J_{PP} = 120.8 Hz, J_{PH} = 530.3, and 17.4 Hz) and +27.16 (J_{PP} = 120.8 Hz, J_{PH} = 7.2, and 19.2 Hz), proving the presence of two diisopropylamino groups on each phosphorus and a proton directly bonded to one of them. A ^{13}C NMR signal of a quaternary carbon appearing at 98.95 as a doublet of doublets ($J_{P(H)C}$ = 143.4 Hz and J_{PC} = 157.9 Hz) confirmed the PCP sequence.

The single-crystal X-ray diffraction study is of primary interest.[8] A ball and stick view of the molecule is shown in Figure 1, as well as the pertinent metric parameters. No interaction with the trifluoromethanesulfonate ion is observed, confirming the ionic
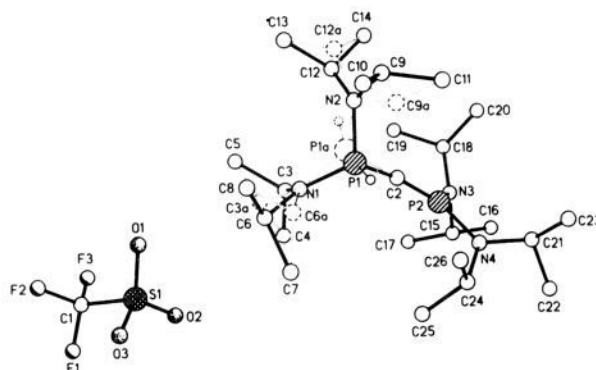
character of **3**. The P(2)–C(2) bond length [1.548 (4) Å] is in the range expected for a phosphorus–carbon triple bond,[3,5] totally excluding a carbene structure of type A. This is confirmed by the planar geometry at P(2) and by the value of the P(1)–C-(2)–P(2) angle [165.1 (4)–164.1 (4)°], which is much larger than that expected for a single carbene (102–105°).[3,9] The [PH-(NR$_2$)$_2$] part of the structure is disordered with sof = 0.62 (1); this is probably due to a facile inversion at the central carbon[3b] along with a free rotation around the P(1)–C(2) bond, which could not be in agreement with structure D. Because of this disorder, the values of the P(1)–C(2) and P(1a)–C(2) bond lengths [1.605 (5) and 1.616 (5) Å] could well not be accurate. A riding model[10] allows us to estimate the lower and upper limits of these bond lengths, which are 1.607 and 1.709 Å, respectively. The SCF equilibrium structure of **3** obtained by employing a flexible split valence plus polarization (SVP) basis[11] led to the following structure constants: P(1)–C(2), 1.698 Å; P(2)–C(2), 1.557 Å; P(1)–C(2)–P(2), 151.2°.[12] The computed bond distances should be accurate to about 0.02 Å and strongly favor the upper limit of the experimental result. In any case, the P(1)–C(2) bond length is by far too short for a phosphorus–carbon single bond, excluding a structure of type B; this is more in the range observed for phosphorus ylides.[13] Lastly, population analyses lead to charges P(1)$^{1.2+}$, C(2)$^{0.9-}$, and P(2)$^{1.1+}$, which strongly favor the electronic structure C.

Although the ^{31}P NMR chemical shifts do not give definite indications of the types of bonding involved, the signal observed for the (phosphanyl)(silyl)carbene [(i-Pr$_2$N)$_2$PCSiMe$_3$] (–40) is shielded compared to that of the nonprotonated phosphorus atom in **3** (+27.16): this is in favor of an increased number of valence bonds at phosphorus. This is not surprising, since the acceptor properties of the silyl group are low compared to those of a phosphonio group, thus favoring a structure closer to B.

In conclusion, phosphanylcarbenes have a highly polarized (P$^{\delta+}$–C$^{\delta-}$) strong phosphorus–carbon multiple bond character.

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(8) Some crystal data for **3**: [C$_{25}$H$_{57}$N$_4$P$_2$]$^+$[CF$_3$SO$_3$]$^-$, M_r = 624.8, yellow crystals, dimensions 0.08 × 0.40 × 0.40 mm; orthorhombic, space group *Pbca* (No. 61), a = 15.859 (1) Å, b = 14.991 (1) Å, c = 29.526 (2) Å, V = 7.020 nm^3, Z = 8, D_c = 1.19 g/cm^3, μ(Cu Kα) = 2.07 mm^{-1}. A total of 4377 symmetry independent reflections ($2\theta_{max}$ = 110°) were recorded at T = 193 K. Of these, 3541 reflections with $|F| > 4\sigma(F)$ were used for the structure solution (direct methods) and refinement (405 parameters). Non-hydrogen atoms were refined anisotropically. R = 0.067 (R_w = 0.069, w^{-1} = $\sigma^2(F)$ + 0.0010F^2). An extinction correction was applied. The [PH(NR$_2$)$_2$] part is disordered [the P(1) and the tertiary C atoms of the *i*-Pr groups, C(2), C(6), C(9), and C(12)] with sof = 0.62 (1).

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Supplementary Material Available: Details of structure determination including tables of crystal and data collection parameters, bond distances and angles with estimated standard deviations, atomic coordinates, anisotropic displacement coefficients, and H-atom coordinates and isotropic displacement coefficients (12 pages); listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

Development of a Gas-Phase Stereochemical Protocol. Intrinsic Diastereoselectivity in Hydride Reductions of Cyclohexanones

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A common feature of classical, intuitive models[1] and modern molecular orbital-based theories[2] for diastereoselectivity in ketone reduction reactions is an emphasis on the structural and electronic properties of the *substrate*, despite the fact that the stereochemical outcome of these reactions often displays marked sensitivity to the solvent and the type of counter-ion employed with ionic and polar reducing agents.[3] One way to separate intrinsic and extrinsic effects on the stereochemistry of ketone reduction reactions is to examine them in the gas phase, where solvent and counterion effects are absent. We describe here an experimental method for distinguishing the *diastereomeric* products of gas-phase hydride reduction reactions, and its application in determining the intrinsic diastereoselectivity involved in reductions of alkyl-substituted cyclohexanones.[4]

Some time ago we reported the generation of pentacoordinate silicon hydride ions in a flowing afterglow instrument from addition of hydride to alkylsilanes (eq 1).[5] These species were found to

$$H^- + RSiH_3 \rightarrow RSiH_4^- \qquad (1)$$

be reactive reducing agents, transferring hydride to CO_2, transition metal carbonyls, boranes, and even to SiH_4.[5-7] With simple aldehydes and ketones, reduction occurs by the net *addition* of an Si–H bond across the carbonyl group to produce an alkoxysiliconate ion (eq 2). The occurrence of C=O reduction is clearly shown by comparing the collision-induced dissociation (CID)

$$BuSiH_4^- + Me_2C=O \rightarrow BuSiH_3(OCHMe_2)^- \leftarrow$$
$$Me_2CHO^- + BuSiH_3 \quad (2)$$
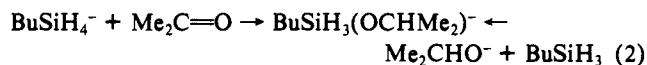
spectrum[4] of the adduct obtained from reaction of $BuSiH_4^-$ with acetone to that obtained from an authentic $BuSiH_3(OCHMe_2)^-$ ion produced by direct addition of Me_2CHO^- to $BuSiH_3$. The spectra measured under similar conditions are indistinguishable,[8] thereby verifying the structural assignment shown for the product of eq 2. Analogous experiments with other alkoxide/carbonyl compound pairs and different alkylsilanes show this behavior to be general.

An alternative approach to siliconate ion reducing agents is the direct addition of a preformed alkoxide ion to a primary, secondary, or tertiary alkylsilane. Reduction of an aldehyde or ketone by the resulting alkoxysiliconate ion then produces a pentacoordinate silicon ion bearing two alkoxy groups (e.g., eq 3). The

$$BuSiH_3 \xrightarrow{RO^-} BuSiH_3(OR)^- \xrightarrow{Me_2C=O}$$
$$BuSiH_2(OR)(OCHMe_2)^- \quad (3)$$
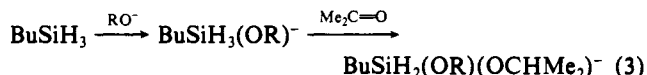
dialkoxysiliconate ions formed in this way provide the keys to determining the diastereoselectivity of the gas-phase reductions. Upon collisional activation, these ions undergo competitive dissociation reactions by loss of the alkoxide ligands. Moreover, the relative yield of the two alkoxides appears to be an extremely sensitive function of their structures and relative basicities. In this sense, dialkoxysiliconate ions are analogous to proton-bound alkoxide dimers $(RO^-)(R'O^-)H^+$, which also undergo competitive alkoxide cleavages with yields reflecting their relative proton affinities.[9] However, the decomposition of dialkoxysiliconate ions appears to be somewhat more sensitive to the *structures* rather than just the basicities of the alkoxy ligands. For example, addition of Me_2CHO^- to $BuSiH_3$ followed by reaction of the adduct with butanal produces the dialkoxysiliconate ion $BuSiH_2$-$(OCHMe_2)(OBu)^-$. CID of this ion with argon target at 12 eV (lab frame) yields the alkoxide fragments in the ratio $Me_2CHO^-/BuO^- = 1.51 \pm 0.15$. For comparison, CID of the corresponding proton-bound dimer $(Me_2CHO^-)(BuO^-)H^+$ under similar conditions gives the alkoxides in essentially identical yields: $Me_2CHO^-/BuO^- = 1.00 \pm 0.01$—a result reflecting their identical Brønsted basicities.[10] Thus, the secondary alkoxide is preferentially cleaved from the siliconate ion, presumably due to steric repulsion effects that weaken the Si–$OCHMe_2$ bond.

The attached ligands in the presumably trigonal–bipyramidal dialkoxysiliconate ions[11] can undergo facile positional exchange, either in the long-lived ions or during CID. This is shown by the equivalence of the CID spectra obtained from the dialkoxy-

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