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Hypersilylphosphanylidene: A Facile Low-Temperature Generation and Formation of Bis(hypersilyl)diphosphene and the Bis(hypersilyl)triphosphaallyl Anion

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Dedicated to Prof. Dr. Reint Eujen on the occasion of his 60th birthday

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The reaction of hypersilyl(trimethylsilyl)chlorophosphane $(SiMe_3)_3SiP(SiMe_3)Cl$ (**1**) with *t*BuOK in THF at –60 °C proceeds by Si–P bond cleavage of the trimethylsilyl group and formation of $tBuOSiMe_3/KCl$ and bis(hypersilyl)phosphanylidene. The phosphanylidene dimerizes to form bis(hypersilyl)diphosphene (**2**) in excellent yields (≥95%). X-ray diffraction experiments reveal the simultaneous presence of two rotamers in the solid state that differ in their SiSiPP torsion angles. Ab initio calculations for the parent diphosphene $(SiH_3)_3SiP{=}PSi(SiH_3)_3$ at the DFT/6-31+G(d) level predict an energy difference of 2.3 $kJ\,mol^{-1}$. A *cis* arrangement of the two $Si(SiH_3)_3$ groups raises the energy by about 45 $kJ\,mol^{-1}$. In the UV/Vis spectrum the $n \rightarrow \pi^*$ excitation is observed at 622 nm, which is in excellent agreement with the ab initio results. In the Raman spectrum, the P=P stretching vibration is easily identified as a strong line at 591 cm^{-1}. When a solution of **1** in THF is added to a solution of KO*t*Bu in THF, maintaining an excess of KO*t*Bu during the reaction, the deep-violet bis(hypersilyl)triphosphenide anion $[HypPPPHyp]^-$ (**4**) forms in excellent yields. This anion is also formed when **2** is treated with KO*t*Bu. Compound **2** can be derivatized with 2,3-dimethylbutadiene to give a cyclic diphosphane **5** by [4+2] addition. When a solution of **2** in toluene is heated to 110 °C for 4 h, bis(hypersilyl)cyclotriphosphane (Hyp_2P_3H, **6**) is formed, besides some $HypPH_2$ as a byproduct. As an aid for the interpretation of ^{31}P NMR spectra, equilibrium structures and phosphorus chemical shifts have been calculated at the DFT and MP2 level for a large number of molecules with phosphorus-containing backbones, which are closely related to those described in the present work. Calculations for disilyldiphosphenes reveal a close correlation between PPSi bond angles and ^{31}P NMR chemical shifts, which is useful for predicting NMR spectra.

Introduction

Over the last two decades a great deal of effort has been devoted to the synthesis of double-bonded systems composed of the heavier elements of group V, such as diphosphenes (RP=PR) and diarsenes (RAs=AsR).[1] Large organic substituents R such as mesityl, supermesityl (2,4,6-tri-*tert*-butylphenyl) or $CH(SiMe_3)_2$ have been used for kinetic stabilisation of the double bonds. Various reactions of these double bonds, such as electrophilic additions or cycloadditions, have also been investigated.

The first disilyldiphosphene, SupP=PSup (Sup = supersilyl = $SitBu_3$) was obtained by Wiberg in 2002 from the reaction of PCl_3 with NaSup. It is formed via $SupPCl_2$ and SupClPPClSup as intermediate products; no crystals suitable for an X-ray investigation could be grown.[2] The same reaction also afforded the bis(supersilyl)triphosphaallyl anion $[SupPPPSup]^-$ a few years earlier, probably via the dianion $[SupPPPPSup]^{2-}$.[3] About ten years before, the synthesis of $[SupAsAsAsSup]^-$ had been described by Jutzi.[4] Both anions could be characterised unambiguously by X-ray diffraction experiments. It is of some note that less bulky silyl groups such as $tBuMe_2Si$ also possess the capability to stabilize unusual structural motifs, for instance SiSi double bonds.[5]

It is a common feature of the chemistry of double bonds between main group elements of period three (and higher) that reactions almost invariably happen at the double bond and not at the substituents, which have to be chosen to be as chemically inert as possible, otherwise they themselves will react with the double bond. The question therefore arises whether substituents can be designed that are large

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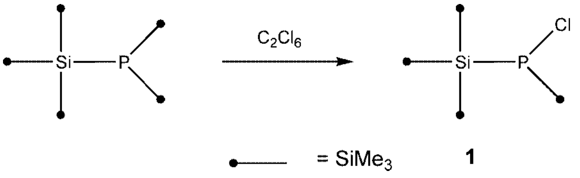
enough to stabilize double bonds but at the same time are sufficiently reactive to allow reactions to be initiated without (at least in the first step) affecting the double bonds. Our experience with oligosilanes led us to the conclusion that oligosilyl groups should be good candidates for this type of substituents for two reasons. First, silyl groups such as $t\mathrm{Bu}_3\mathrm{Si}$ can be used successfully for the stabilisation of double bonds (as Wiberg has shown), which supports the idea that oligosilyl groups can serve the same purpose. Second, SiSi bonds readily undergo cleavage reactions under relatively mild conditions, even at low temperatures. In the present publication we explore a method that can be used for the preparation of oligosilylphosphanylidenes, bis(oligosilyl)diphosphenes and bis(oligosilyl)triphosphaallyl anions. The method can probably be used for organo-substituted phosphanylidenes as well. The hypersilyl group $\mathrm{Si(SiMe_3)_3}$ (denoted as Hyp) was chosen to demonstrate the feasibility of the reactions because it is easily and quickly accessible in large quantities. We will report on the results using other oligosilyl groups in a forthcoming paper.

Results and Discussion

One of the problems one faces when attempting to prepare silylated diphosphenes is that silyl groups are excellent leaving groups in phosphorus chemistry. For instance, $\mathrm{SiMe_3}$ groups are routinely used for the preparation of organodiphosphenes RP=PR by elimination of chlorotrimethylsilane from $\mathrm{RPCl_2}$ and $\mathrm{RP(SiMe_3)_2}$.[6] The question therefore is whether the reaction rates of oligosilyl groups differ sufficiently from those of trimethylsilyl groups to open new paths to tailored diphosphenes. A slower reaction rate of the hypersilyl group would make the synthesis of the hypersilylphosphanylidene and of bis(hypersilyl)diphosphene an accessible goal. Silylphosphanylidenes such as $\mathrm{H_3SiP}$ are computed to prefer the triplet ground state by 122 kJ mol^{-1} (CASSCF/6-31G** level).[7] At the QCISD(T)/6-311++G(3df2p)//UMP2/6-31G** level, this energy reduces to 107 kJ mol^{-1}.[7b] The triplet structure is stable towards rearrangement into the phosphasilene with a barrier of 170 kJ mol^{-1} and a relative energy of the product of 61 kJ mol^{-1}. Therefore, a migration of the trimethylsilyl group in triplet $\mathrm{(SiMe_3)_3SiP}$ to form $\mathrm{(SiMe_3)_2Si{=}P(SiMe_3)}$ is unlikely to occur.

Synthesis

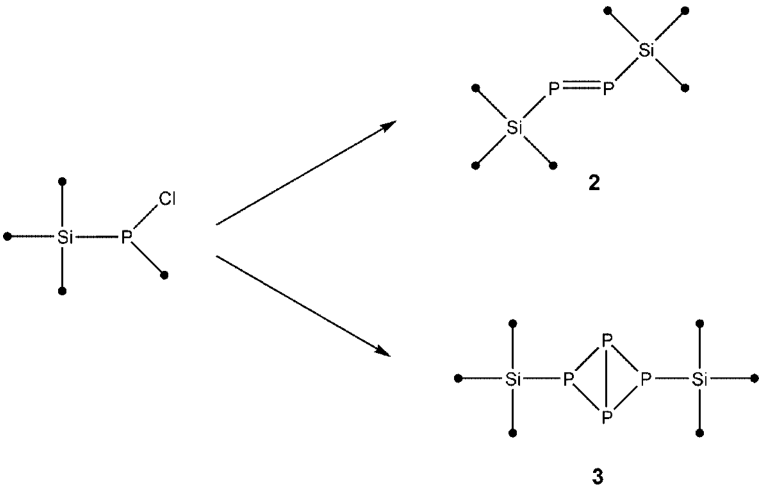
As reported elsewhere, $\mathrm{(SiMe_3)_3SiP(SiMe_3)_2}$ reacts with $\mathrm{C_2Cl_6}$ to form a stable chlorodisilylphosphane **1**, as shown in Scheme 1.[8]



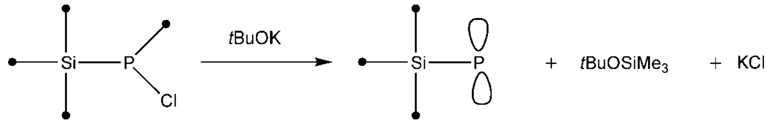
Scheme 1.

A solution of **1** in toluene does not decompose at room temperature or if heated at 90 °C for 2 h, but does so in refluxing toluene (110 °C) with formation of chlorotrimethylsilane and a plethora of compounds, although without any indications of a PP double bond. In contrast, the pure, colourless chlorodisilylphosphane turns light green at 20 °C over a period of a week, and bis(hypersilyl)diphosphene (**2**) can be identified in the reaction mixture by ^{31}P NMR spectroscopy along with bis(hypersilyl)bicyclotetraphosphane (**3**), as shown in Scheme 2.

From the ^{31}P NMR spectrum it follows that **2** and **3** form in a ratio of about 2:1, with **2** giving a single line at δ = 735.0 ppm (as compared to δ = 818.1 ppm for SupP=PSup). The spectrum of **3** is of first-order ($\mathrm{A_2X_2}$) and consists of two triplets at δ = –329.2 and –155.0 ppm with a $^{1}J_{\mathrm{P,P}}$ coupling constant of 161.8 Hz, which clearly demonstrates that it is the *exo*/*exo* isomer that is formed exclusively. The *exo*/*endo* isomer is expected to give more signals, and the formation of the *endo*/*endo* isomer is extremely unlikely due



Scheme 2.



Scheme 3.

to the steric interactions of the large hypersilyl groups. It is worth noting that the analogous supersilyl compound Sup_2P_4 has also been observed by Wiberg in the reaction between $SupPCl_2$ and NaSup (δ = –334.4 and –139.1 ppm, ${}^1J_{P,P}$ = 170.5 Hz).[2]

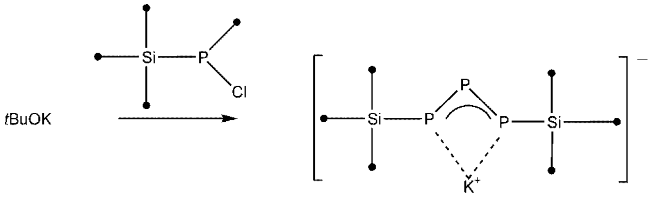
Besides **2** and **3**, the decomposition of **1** also affords trihypersilylheptaphosphane (P_7Hyp_3) as well as a second P_n cage or polycycle of as-yet-unknown structure with second-order resonances between δ = –90 and –220 ppm as minor by-products.

The observed reaction products suggest that under these conditions the diphosphene is formed by dimerisation via HypClP–P($SiMe_3$)Hyp and subsequent elimination of chlorotrimethylsilane. A possible reaction pathway leading to the formation of the diphosphane would be the insertion of hypersilylphosphanylidene (formed from **1** by 1,1-elimination of chlorotrimethylsilane) into the PCl bond of **1**. The occurrence of reaction products such as Hyp_2P_4 and Hyp_3P_7 indicates that under these conditions the SiP bond of the hypersilyl group also takes part in the reaction, albeit with a much lower reaction rate.

These considerations led us to the expectation that the dimerisation of hypersilylphosphanylidene to form the diphosphene would be the preferred reaction if the phosphanylidene could be generated quickly and in quantitative yield. This is easily achieved by reaction of **1** with KO*t*Bu, to form the phosphanylidene, *t*BuOSiMe$_3$ and KCl, as shown in Scheme 3. Previously we have shown that KO*t*Bu can indeed be used to cleave an SiP bond of $P(SiMe_3)_3$,[9] and that the reaction with $HypP(SiMe_3)_2$ proceeds quickly and selectively with formation of *t*BuOSiMe$_3$ and HypP($SiMe_3$)K.[8] The reaction rate of the hypersilyl group is much slower.

When a solution of KO*t*Bu in THF is added to a solution of HypPCl($SiMe_3$) in THF very slowly at –60 °C to avoid any local excess of the reagent, light-green **2** forms quantitatively (≥95%, by ^{31}P NMR) without any noticeable by-products. Compound **2** crystallises readily from pentane. The exclusive formation of the diphosphene **2** strongly supports the idea that the reaction indeed proceeds via hypersilylphosphanylidene. Compared to other methods described in the literature that can be used to prepare phosphanylidenes, its generation from RP($SiMe_3$)Cl and KO*t*Bu can be achieved at much lower temperatures. For instance, the phosphoranylidenephosphane *t*Bu$_2$P–P=PBr(*t*Bu)$_2$ decomposes at 20 °C to give the phosphanylphosphanylidene *t*Bu$_2$PP, which has been trapped with 2,3-dimethylbutadiene.[10] The generation of phosphanylidenes from three-membered rings requires even higher temperatures of up to 140 °C.[11]

During these experiments we noticed that if the two solutions are mixed very quickly, the colour immediately changes to a dark-brown, which then slowly turns into a dark-violet. We therefore reversed the reaction sequence described above, adding the solution of HypPCl($SiMe_3$) to the solution of KO*t*Bu, maintaining an excess of KO*t*Bu throughout the whole procedure. In this way potassium 1,3-bis(hypersilyl)triphosphenide (**4**) can be obtained almost quantitatively (≥90%, by ^{31}P NMR), as shown in Scheme 4.



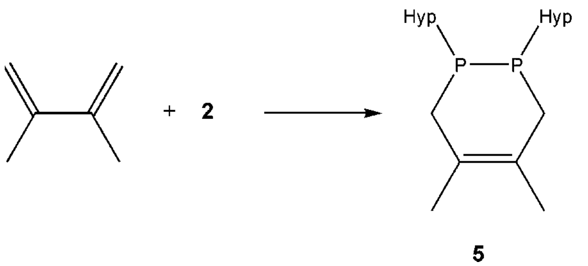
4

Scheme 4.

The ^{31}P NMR spectrum of **4** consists of a triplet at δ = 705.5 ppm and a doublet at δ = 197.5 ppm with a coupling constant of 540.4 Hz; values of δ = 732.5, 212.5 ppm and 552.6 Hz have been reported for the analogous supersilyl derivative.[3] Attempts to crystallise **4** as the [18-crown-6·K]$^+$ salt were not successful.[12] Our experiments showed that treating HypP=PHyp with KO*t*Bu also led to the formation of **4**. Whether the reaction starts with SiP or SiSi bond cleavage remains unknown; the mechanism is under investigation.

Derivatisation of 2 and 4

When 2,3-dimethylbutadiene is added to a solution of **2** in toluene, the green colour disappears slowly with formation of the [4+2] cycloaddition product **5**, which was identified by NMR spectroscopy. The ^{31}P nuclei give a singlet at δ = –137.6 ppm, and the ^{29}Si NMR spectrum consists of two pseudotriplets at δ = –9.8 ($SiMe_3$ groups) and –89.5 ppm (see also Experimental Section). The reaction proceeds quantitatively.



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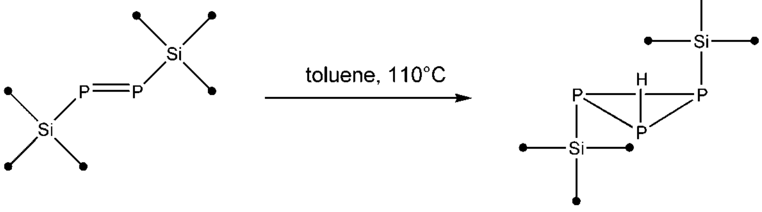

2 **6**

When **4** reacts with trifluoroacetic acid, bis(hypersilyl)cyclotriphosphane Hyp_2P_3H (**6**) forms almost quantitatively, along with some hypersilylphosphane $HypPH_2$. We were not able to obtain crystals suitable for X-ray diffraction, therefore **6** was characterised by ^{31}P NMR spectroscopy, including 2D-COSY experiments. Remarkably, **6** also forms when a solution of **2** in toluene is refluxed for several hours. Here again, the major by-product is hypersilylphosphane, which cannot be removed quantitatively by sublimation in vacuo as **6** decomposes slowly upon raising the temperature. A solution of **2** in THF does not decompose, even if held under reflux for 6 h.

The ^{31}P and $^{31}P\{^1H\}$ NMR spectra and the COSY spectrum of the cyclotriphosphane are illustrated in Figure 1 (left and right, respectively). The $^{31}P\{^1H\}$ NMR spectrum exhibits signals of an AMP spin system [$\delta_A(P^1)$ = –233.0, $\delta_M(P^2)$ = –241.3, $\delta_P(P^3)$ = –260.9 ppm; $^1J_{P^1,P^2}$ = –142.1, $^1J_{P^1,P^3}$ = –202.3, $^1J_{P^2,P^3}$ = –182.7 Hz]. The larger coupling between P^1 and P^3 indicates a *cis* orientation of the substituents H and Hyp. In the proton-coupled spectrum, the AMP spin system extends to AMPX [$^1J_{P^1,H}$ = 141.1Hz, $^2J_{P^2,H}$ = 10.0, $^2J_{P^3,H} < 3$ Hz]. A calculated $^{31}P\{^1H\}$ spectrum assuming negative values for all P–P coupling constants is also included as (c) in Figure 1 (left).

X-ray Crystallography

An ORTEP plot of the molecular structure of **2** in the crystal as well as the numbering of the atoms is presented in Figure 2; selected bond lengths, bond angles and torsion angles are collected in Table 1. As expected, it is the *trans* isomer that is formed by dimerisation of the phosphanylidene. Surprisingly, two stereoisomers **A** and **B** that differ by a rotation of the hypersilyl group around the PSi bond are observed in the crystal. If viewed along an axis joining the two central Si atoms of the hypersilyl groups, the trimethylsilyl groups in isomer **A** are in a staggered arrangement with dihedral angles between 55° and 65°. The molecule possesses an inversion centre. In isomer **B**, the arrangement of the trimethylsilyl groups is almost eclipsed with the dihedral angles alternating between 5° and 120°, giving approximately a C_s-symmetric isomer with differences between the PSiSi and SiSiSi bond angles on both sides of the molecule being smaller than about 2° (Table 1). As described later on, the ab initio calculations for $(SiH_3)_3SiP{=}PSi(SiH_3)_3$ also predict two minima on the potential energy surface corresponding to **A** and **B**. At the level employed for these calculations [B3LYP/6-31+G(d)], **B** becomes a transition structure for $(SiMe_3)_3SiP{=}PSi(SiMe_3)_3$. Obviously, it is stabilized in the crystal due to packing effects.

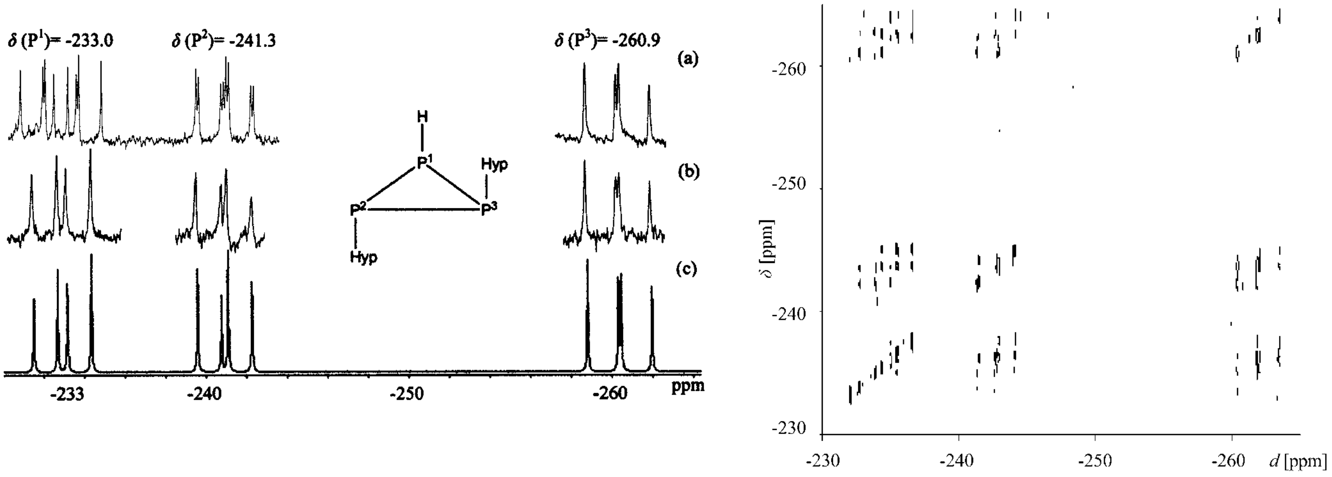

Figure 1. Left: Proton-coupled (a), decoupled (b) and calculated (c) ^{31}P NMR spectrum of bis(hypersilyl)cyclotriphosphane (**6**). Right: ^{31}P COSY spectrum of **6**.

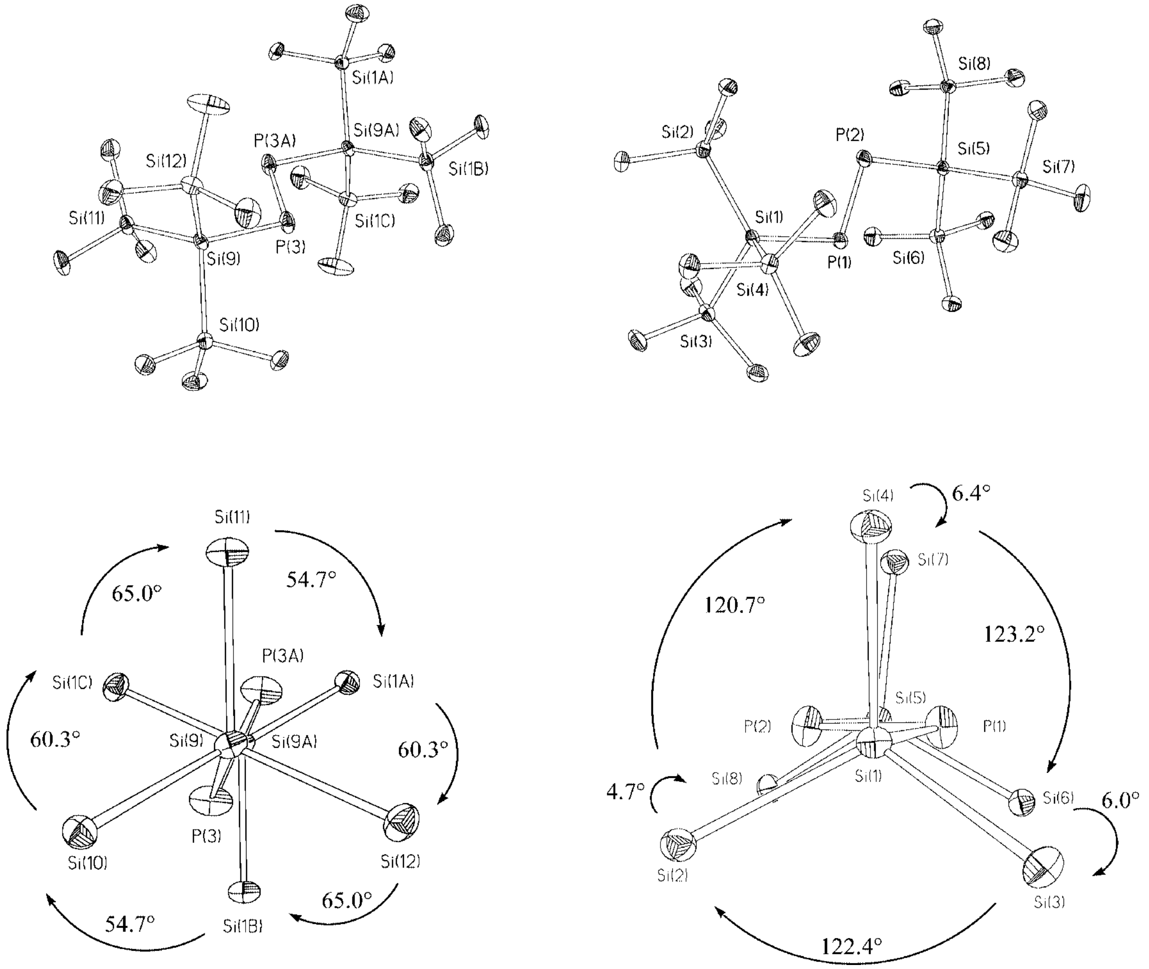

Figure 2. ORTEP plots of the two conformers of bis(hypersilyl)diphosphene in the crystal (top) and projections showing the different dihedral angles between the $SiMe_3$ groups (bottom). Isomer **A** is on the left and isomer **B** on the right side.

Table 1. Selected bond lengths [pm], bond angles [°] and dihedral angles [°] for the two isomers **A** and **B** of bis(hypersilyl)diphosphene.

	Isomer **A**	Isomer **B**
PP	203.0(2)	202.2(2)
PSi	228.0(2)	227.0(2), 226.9(2)
SiSi	234.6(2), 235.0(2), 235.3(2)	234.6(2), 234.6(1), 235.0(2) 234.4(2), 234.9(2), 235.5(2)
PPSi	102.7(1)	103.2(1), 100.9(1)
PSiSi	106.0(1), 104.4(1), 115.6(1)	100.9(1), 104.7(1), 114.1(1) 103.1(1), 106.7(1), 113.5(1)
SiSiSi	107.8(1), 110.9(1), 111.6(1)	111.0(1), 111.6(1), 113.7(1) 111.0(1), 109.9(1), 112.3(1)
SiPPSi	180.0	–178.2(2)

The P=P bond lengths of isomer **A** [203.0(2) pm] and **B** [202.2(2) pm] are almost identical, which is also the case for the PSi and SiSi bonds. Moreover, all distances are in the range that is considered normal for P=P, P–Si and Si–Si bonds and need no further discussion.

Raman and UV Spectra

As diphosphenes possess absorptions in the UV and visible range (usually assigned as π–π* and n–π* transitions), the Raman spectra obtained with excitation sources in the visible or UV range are expected to show resonance or pre-resonance effects. The two main effects are an intensity enhancement as well as the appearance of an overtone progression for the P=P stretching vibration. So far, wavenumbers for the P=P stretch have been determined for $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ ($595\ cm^{-1}$) and ArP=PAr [Ar = 2,4,6-tri-*tert*-butylphenyl ($610\ cm^{-1}$) and 2,6-bis(*m*-xylyl)-phenyl ($622\ cm^{-1}$)].[13] There seems to be only a limited amount of mixing between the P=P and P–C stretching vibrations despite the fact that they are quite close to each other. This was concluded from a normal coordinate analysis (NCA) of MeP=PMe and $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ by treating the methyl group as a point mass of 15.[14] So far, no NCA for a diphosphene based on an ab initio force field has been reported in the literature.

The Raman spectrum of bis(hypersilyl)diphosphene in the wavenumber range 50–900 cm^{-1} is presented in Figure 3. The green 532-nm line of a frequency-doubled Nd:YAG laser (10 mW) was used to excite the sample. Its interpretation is rather straightforward, even without a NCA.

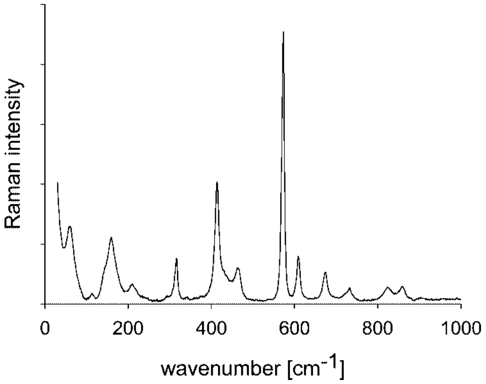

Figure 3. Raman spectrum of solid bis(hypersilyl)diphosphene in the wavenumber range 50–900 cm^{-1}.

The strongest line in this range, at 591 cm^{-1}, is clearly the P=P stretch, with the symmetric SiC_3 stretch at 626 cm^{-1} being quite close. Nevertheless, there is negligible kinetic coupling between these two modes because the SiC bonds are separated from the P=P double bond by two SiSi bonds. This is not the case for the PSi and SiSi modes, which are expected on the low-wavenumber side in the range 300–500 cm^{-1}. They are observed at 481 and 450 cm^{-1} [$\nu_{as}(SiSi_3)$], 431 cm^{-1} [ν(PSi)] and 332 and 323 cm^{-1} [$\nu_s(SiSi_3)$]. The SiSiC and CSiC deformations of the trimethylsilyl groups fall in the range 50–240 cm^{-1}. No line splittings due to the presence of the two isomers **A** and **B** is observed as their spectra are expected to differ very little. This is confirmed by the ab initio results for the parent molecule $(SiH_3)_3SiP{=}PSi(SiH_3)_3$ (see next section).

For corroboration of the assignments given above, a normal coordinate analysis was carried out for $(H_3Si)_3SiP{=}PSi(SiH_3)_3$ and $(Me_3Si)_3SiP{=}PSi(SiMe_3)_3$ employing the Hessian matrices obtained from ab initio calculations (see next section). The Hessian matrix gives the force constants defined as displacements of Cartesian coordinates and has to be transformed into a force field described in terms of symmetry coordinates that themselves are linear combinations of displacements of internal coordinates such as bond lengths, bond angles and torsion angles. These calculations, known to spectroscopists as Wilson's FG method,[15] were performed using an enlarged version of the program ASYM40.[16] ASYM40 needs the Hessian matrix and the atomic coordinates of the equilibrium geometry as input data as well as the symmetry coordinates, which were chosen according to standard methods described in the literature.[17] Calculated PP, SiP and SiSi stretching force constants are summarised in Table 2. The P=P force constant is predicted as 326 and 332 N m^{-1} for $(H_3Si)_3SiP{=}PSi(SiH_3)_3$ and $(Me_3Si)_3SiP{=}PSi(SiMe_3)_3$, respectively. The force constant for a PP single bond, for instance in $(SiMe_3)_2PP(SiMe_3)_2$, is considerably smaller, a value of 195 N m^{-1} being obtained from ab initio calculations on this molecule.[18] Furthermore, the calculations of the potential energy distributions (PED) show that ν(P=P) is indeed a group vibration in these diphosphenes, with *f*(PP) contributing as much as 86% to ν(P=P) in $(H_3Si)_3SiP{=}PSi(SiH_3)_3$ and 97% in $(Me_3Si)_3SiP{=}PSi(SiMe_3)_3$. Coupling with other modes can be largely neglected.

Table 2. Experimental and calculated wavenumbers [cm^{-1}] for the PP and in-phase SiP and SiSi stretching vibrations and calculated force constants [N m^{-1}] for the rotational conformers **A**, **B** and **C** of $H_9Si_4P{=}PSi_4H_9$ [B3LYP/6-311+G(d)] and **A** of $Me_9Si_4P{=}PSi_4Me_9$ [B3LYP/6-311+G(d)].

	$(H_3Si)_3SiP{=}PSi(SiH_3)_3$			$(Me_3Si)_3SiP{=}PSi(SiMe_3)_3$	
	A	**B**	**C**	**A**	
	calcd.	calcd.	calcd.	calcd.	exp.
ν(P=P)	603	599	597	604	591
ν(PSi)	415	416	391	433	431
$\nu_s(SiSi_3)$	314	314	278	331	332
$\nu_{as}(SiSi_3)$	437	433	424	479	481
f(P=P)	326			332	
f(PSi)	153			157	
f(SiSi)	157			157	

The UV/Vis spectrum of **2** (solution in *n*-hexane) is presented in Figure 4 for three different concentrations. The absorption maxima corresponding to π→π* and n→π* excitations appear at 400 and 622 nm, respectively, the latter of which causes the green colour (see section on ab initio calculations).

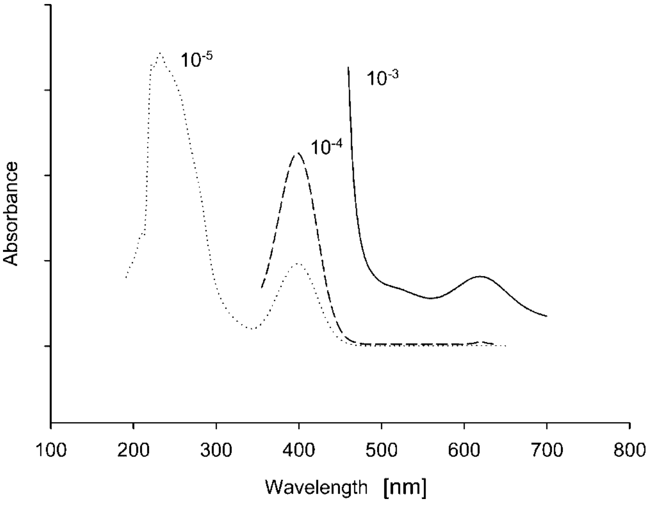

Figure 4. UV/Vis spectrum of bis(hypersilyl)diphosphene (**2**) for concentrations of 10^{-5}, 10^{-4} and 10^{-3} M.

Ab initio Calculations

Bis(hypersilyl)diphosphene

Hyp–P=P–Hyp (**2**) is, with 82 atoms, computationally quite demanding. For our calculations at the B3LYP/6-31+G(d) level, we first used a smaller model created by replacing the hypersilyl groups by $Si(SiH_3)_3$.

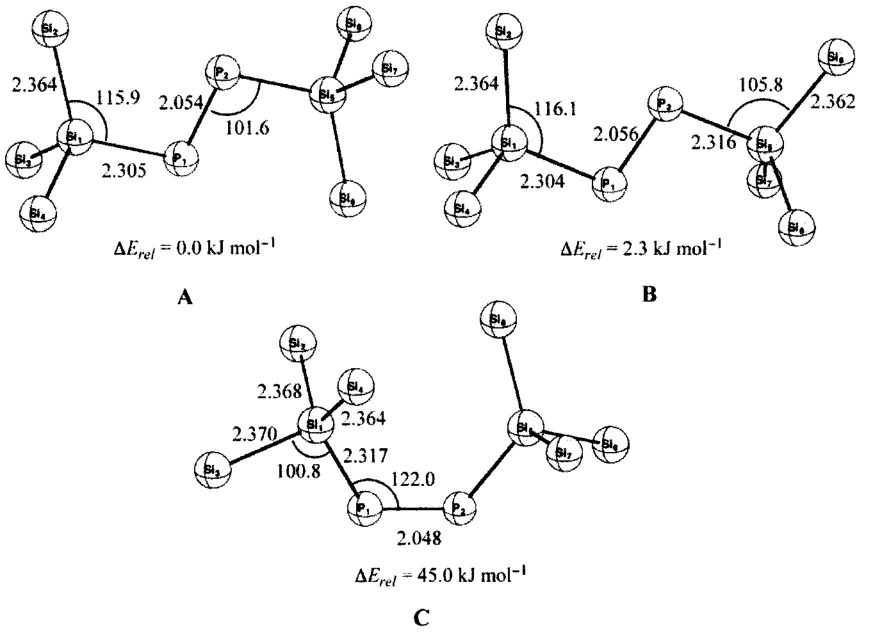

Figure 5. Rotational isomers of $(H_3Si)_3Si–P=P–Si(SiH_3)_3$ at the B3LYP/6-31+G(d) level of theory. The hydrogen atoms have been omitted for clarity.

Three minima were located on the potential energy surface (PES), as depicted in Figure 5.

The low-energy minima **A** and **B** have the Si–P=P–Si backbone in a *trans* orientation corresponding to the structures identified by X-ray spectroscopy. The energy separation (ΔE_{rel} = 2.3 kJ mol^{-1}) is quite small. The SiH_3 groups in **A** are oriented *trans* to each other and the conformer possesses a centre of inversion. The reason for the higher stability of this geometric arrangement can be identified by NBO analyses. Negative hyperconjugation occurs between the P lone pair and the respective antibonding Si–Si orbital if the SiH_3 group is oriented *cis* to the P=P double bond. Rotation of one $Si(SiH_3)_3$ group around the P–Si bond until the $H_3Si–Si–P–P$ angle is 180° yields the C_s-symmetric minimum **B**, destroys one of the LP(P)→σ*(Si–Si) interactions and consequently diminishes the stability.

The negative hyperconjugation also affects the bond lengths and angles. The P–Si bond length shrinks by 0.01 Å and the respective P–Si–Si angle becomes wider. For the full geometry data, see the Supporting Information.

A *cis* orientation of the Si–P=P–Si backbone is quite unfavourable and only one minimum, **C**, with a relative energy of 45.0 kJ mol^{-1} was located on the PES.

The P=P stretching vibrations of the three minima [603 (**A**), 599 (**B**) and 597 cm^{-1} (**C**)] are too close to discern the conformers by Raman spectroscopy. The same is true for the ν(PSi), $\nu_s(SiSi_3)$ and $\nu_{as}(SiSi_3)$ vibrations listed in Table 2.

As the synthesised diphosphene is light-green, we calculated UV/Vis spectra with time-dependent B3LYP and 6-311+G(d) basis sets. The global minimum has a strong absorption band at 358 nm (f = 0.27) corresponding to a π → π* excitation. The HOMO–LUMO transition, corresponding to an n → π* excitation, is found at 562 nm but should not be visible as the oscillator strength is 0.00. However, the oscillator strength of the same transition for minimum **B** at 583 nm is calculated to be 0.0002. There is also a strong π → π* transition at 367 nm (f = 0.21). Minimum **C** shows a similar behaviour, with a weak n →π* excitation at 586 nm (f = 0.0002) and a strong π → π* transition at 359 nm (f = 0.13).

Upon replacment of $Si(SiH_3)_3$ by the full hypersilyl group $Si\{Si(CH_3)_3\}_3$, only structure **A** corresponds to a minimum, while **B** becomes a transition structure at the B3LYP/6-31+G(d) level used. Due to space limitations, we were unable to perform MP2 calculations, which might predict **B** to be a minimum structure, too. The geometric parameters change slightly due to the larger hypersilyl groups. The P=P distance remains at 2.054 Å, but the P–Si bonds elongate by 0.01 Å and the SiPP bond angles become 4° wider. The characteristic Raman frequencies are close to the values of the smaller model, as shown in Table 2.

As expected, the n → π* excitation drifts to larger wavelengths, namely 632 nm. However, as for the smaller model, this HOMO–LUMO transition for **A** is not visible (f = 0.0), although the π → π* excitation at 409 nm is quite strong (f = 0.24).

Bis(hypersilyl)triphosphenide

We also performed ab initio calculations for the bis(hypersilyl)triphosphenide anion at the same level of theory [B3LYP/6-31+G(d)], including calculations of ^{31}P chemical shifts. The C_2-optimised structure is shown in Figure 6. The Si–Si–P bond angle is only 3° wider in the Hyp_2P_3 anion than in $[(H_3Si)_3Si]_2P_3$ and about 8° wider than in the parent $(H_3Si)_2P_3$ (**10a**; see next section). Nevertheless, the P–P–P angle of the allylic backbone is roughly identical for R = Hyp (Figure 6) and $Si(SiH_3)_3$ (106.1°), and only 3° narrower than in the parent. Even though the formal cone angle of hypersilyl is approximately 180°, the P–P–Si arrangement is far from linear. Therefore, investigations of the variation of the steric effect of R are of ongoing interest. A comparison of the DFT-calculated NMR chemical shifts (Figure 6) shows that the values are much too positive. When the correction factor 0.84, which is described in the section "^{31}P NMR Shift Calculations", is considered, the shift of the signal of the central phosphorus atom is δ = 695 ppm, in agreement with the observed value of δ = 705 ppm. For the terminal phosphorus atoms, which have a direct contact with the counterion, the correction leads to a value of δ = 229 ppm, which differs by only about 11 ppm from the experimental value.

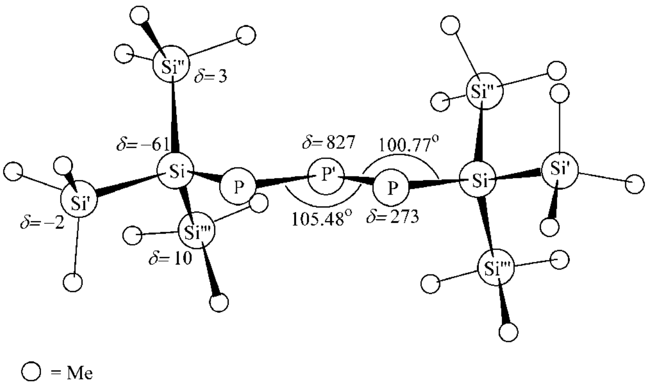

Figure 6. Optimized C_2 geometry for bis(hypersilyl)triphosphenide.

Geometries of Model Compounds

To gain a deeper understanding of the steric and electronic influences of the substituents on the structures of molecules with phosphorus-containing backbones, geometry optimisations at the B3LYP/6-31+G* level of theory were performed for **7**–**12**, as shown in Figure 7. The model compounds, which are closely related to compounds **2**–**6**

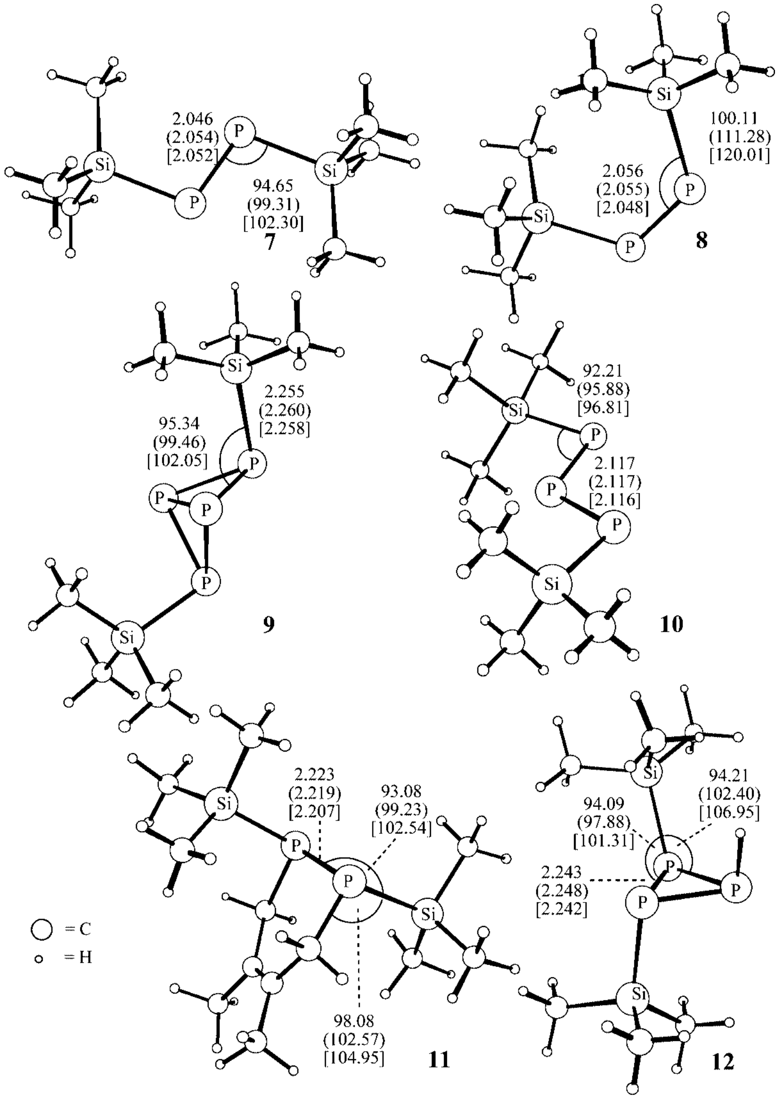

Figure 7. Ab initio (B3LYP/6-31+G*) optimised geometries of molecules with phosphorus-containing backbones (**7**–**12**). Structures for R = H and R = SiH_3 are not depicted. Values are given for R = H, with those for R = SiH_3 in parentheses and for R = $Si(CH_3)_3$ in square brackets.

described previously, were *trans*-RP=PR (R = H, **7a**; R = SiH_3, **7b**; R = $SiMe_3$, **7c**), *cis*-RP=PR (**8a**–**8c**), R_2P_4 (**9a**–**9c**), $[R_2P_3]^-$ (**10a**–**10c**), $R_2(PCH_2CHMe)_2$ (**11a**–**11c**) and R_2P_3H (**12a**–**12c**). The backbones in this set vary from common tricoordinate phosphorus (**9**, **11** and **12**) through phosphorus in an allyl anion framework (**10**) to the P=P double bond in **7** and **8**.

The selected R groups differ only slightly in their inductive effects towards phosphorus, as seen by the Mulliken charges of RPH_2, which are –0.03 for R = H, –0.05 for SiH_3 and –0.06 for $SiMe_3$. The π-conjugation effect, as expressed by the bond angle sum, Σa, at PH_2[19] is difficult to separate from steric influences measured by the cone angle, γ, of R with P as the cone point.[20] The average cone angles (80.24° for R = H, 94.32° for SiH_3 and 125.16° for $SiMe_3$) derived from the //B3LYP/6-31+G* geometries suggest that silyl and trimethylsilyl should show distinctly different steric effects.

In the bicyclotetraphosphanes **9** as well as in the cyclotriphosphanes **12** the substituents R are attached to a P_3 ring. The SiH_3 substituent has the largest elongating effect on the P^{α}–P bond, and the R–P^{α}–P angle increases from H through SiH_3 to $SiMe_3$ (see Figure 7), paralleling the increase of the cone angles. While the R–P^{α}–P and R–P^{α}–C bond angles increase similarly in the six-membered ring **11**, the P–P bond length shrinks with silylation (H: 2.223; SiH_3: 2.219; $SiMe_3$: 2.207 Å). The allyl anions **10a**–**10c** with a delocalised π-conjugation show astonishing population effects on the phosphorus atom attached to R with charges –0.27 (H), –0.29 (SiH_3) and –0.21 ($SiMe_3$). H and SiH_3 behave more similarly than SiH_3 and $SiMe_3$. In contrast, the charges of the central P atom follow the trend of the inductive effect (–0.36, –0.16 and –0.18, respectively). The P–P bond length is almost unaffected by the substituents, and the P–P–P angle is smaller in the silyl derivatives, with a range of 107.30–108.58°. Counterion effects on the geometry of the triphosphaallyl anion have been discussed elsewhere.[3]

Compared to the allyl bond length, the P=P double bond is modified slightly more by the substituents, with values of 2.046, 2.054 and 2.052 Å for the *trans*-diphosphenes **7a**–**7c** and 2.056, 2.055 and 2.048 Å for the *cis*-diphosphenes **8a**–**8c**. Substantial changes are obtained for the R–P–P angles, which are 94.65°, 99.32° and 102.30° for the *trans* isomers. Due to the steric interaction between the substituents, these values are much larger for the *cis* isomers (106.11°, 111.28° and 120.01°). It is also noteworthy that the R–P–P–R torsion angles always differ by less than 1° from 180° (*trans*) or 0° (*cis*), even in *cis*-$Me_3SiP{=}PSiMe_3$.

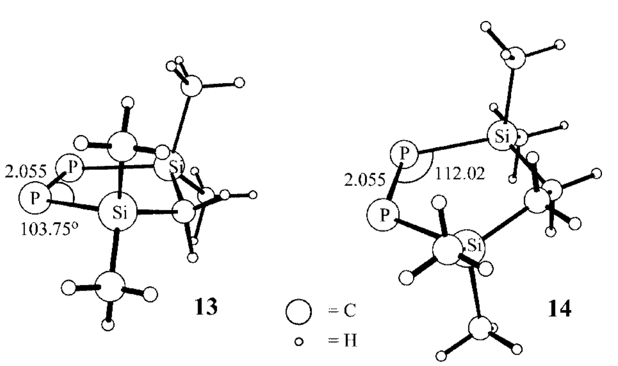

Figure 8. Geometries for model compounds **13** and **14**.

The model compounds also include two silylated cyclic diphosphenes, which possess a *cis* geometry of the double bond, as shown in Figure 8.

^{31}P NMR Shift Calculations

The ^{31}P chemical shifts of supersilyldiphosphene and hypersilyldiphosphene differ by a striking 83 ppm. The difference is much smaller for other isostructural hypersilyl and supersilyl compounds such as R_2P_4 or R_2P_3H and the allyl anion $[R_2P_3]^-$, at less than 25–30 ppm. As both SupP=PSup and HypP=PHyp are too large for high-quality MP2 shift calculations, we have performed a series of calculations for smaller diphosphenes as a test for the accuracy of the DFT calculations. Table 3 lists the chemical shifts for a series of selected diphosphenes (including cyclic derivatives with a *cis* arrangement) calculated at the DFT and various MP2 levels. We employed the B3LYP method with the 6-31G* basis set and the MP2 method with the three basis sets 6-31G* and McLean–Chandler's 6-311G* and 6-311+G**, labelled B3LYP-A, MP2-A, MP2-B and MP2-C further on. From the correlation analysis, the equation $\delta_{^{31}P(MP2\text{-}C)} = 0.84 \times \delta_{^{31}P(DFT\text{-}A)}$, which has a negligible intercept and squared correlation coefficient, *cc*, of 0.984, is obtained. Thus, ^{31}P chemical shifts can be reliably estimated with this equation from DFT results. The correlation also extends to tetracoordinate phosphorus, as shown by including calculations for $[PH_3PH_2]^+$.

The DFT-A calculations with C_1 symmetry predict $\delta_{^{31}P}$ = 917 ppm for HypP=PHyp and 1071 ppm for SupP=PSup. The difference of 154 ppm becomes 129 ppm when taking into account the correlation mentioned above, thus increasing the agreement with the experimental difference (83 ppm).

We next turned to the question as to whether differing PPSi bond angles can cause large shift differences. The DFT-A calculations provide values of 104.55°/104.54° for HypP=PHyp (somewhat larger than the experimental values, see Table 1) and 106.47°/106.60° for SupP=PSup. To search for a bond angle–chemical shift relationship, DFT-A calculations were performed for ten *cis*- and twenty *trans*-RP=PR molecules. The predicted $\delta_{^{31}P}$ values are plotted as functions of the R–P=P angle, a, for a large variety of R groups, such as H, F, Cl, CF_3,CH_3, *t*Bu, NH_2, NMe_2, SiH_3 and $SiMe_3$, in Figure 9. Several cyclic diphosphenes with PC, PN and PSi bonds are also included (see Table 3). In agreement with previous investigations,[21] a regression analysis confirms the impression that there is no general relationship that is valid for all substituents ($cc < 0.2$). Nevertheless, some subsets do display interesting trends that are useful for predicting phosphorus shifts. The data points for the substituents H, F, SiH_3, $SiMe_3$, Hyp and Sup correlate nicely with the calculated bond angles with the linear fit $\delta_{^{31}P} = 37 + 2866a$ (cc = 0.966). Small changes of the PPSi

Table 3. Chemical shifts at the DFT and MP2 levels for *cis*-R–P=P–R and the $H_3P^*PH_2^+$ cation.

R	DFT-A[a,b]	MP2-A[a]	MP2-B[a]	MP2-C[a]
H	587	395	488	466
Cl	698	470	555	540
F	754	574	672	660
CH_3	595	425	516	500
*t*Bu	640	474	562	554
SiH_3	791	545	632	616
$SiMe_3$	875	605	694	680
CF_3	583	409	481	476
cyclo-(NH)–P=P*–$(CH_2)_2$[c]	299	207	270	272
cyclo-(NH)–P*=P–$(CH_2)_2$[c]	484	363	444	437
cyclo-P=P–$(CH_2)_3$[c]	570	424	509	497
cyclo-P=P–$(CH_2)_4$[c]	526	403	487	478
cyclo-(NH)–P=P–(NH)–(CH_2)[c]	366	267	336	337
cyclo-(NMe)–P=P–(NMe)–(CH_2)[c]	369	273	340	342
$H_3PP^*H_2^+$	–187	–201	–187	–192
$H_3P^*PH_2^+$	–111	–117	–109	–107

[a] All molecules optimised without symmetry constraints at the B3LYP/6-31G* level. Chemical shifts calculated for these geometries at the GIAO/B3LYP/6-31G* (DFT-A) and GIAO/MP2(fc) with 6-31G* (MP2-A), 6-311G* (MP2-B) and 6-311+G** (MP2-C) levels. Reference PH_3 with the same NMR methods at the //B3LYP/6-31+G* level has magnetic shieldings of 585.6 (DFT-A), 646.2 (MP2-A), 613.6 (MP2-B), 607.1 (MP2-C) and a chemical shift of δ = –240 ppm. [b] The slope and squared correlation coefficient, *cc*, between $\delta_{^{31}P(DFT\text{-}A)}$ and the higher levels of NMR calculation are: $\delta_{^{31}P(MP2\text{-}A)} = 0.77\delta_{^{31}P(DFT\text{-}A)} - 31$ ppm, with $r = 0.989$; $\delta_{^{31}P(MP2\text{-}B)} = 0.86\delta_{^{31}P(DFT\text{-}A)} + 0$ ppm, with $r = 0.988$; and $\delta_{^{31}P(MP2\text{-}C)} = 0.84\delta_{^{31}P(DFT\text{-}A)} + 0$ ppm, with $r = 0.984$. [c] Cyclic compounds with a *cis* arrangement of the P=P double bond; otherwise *trans* conformer.

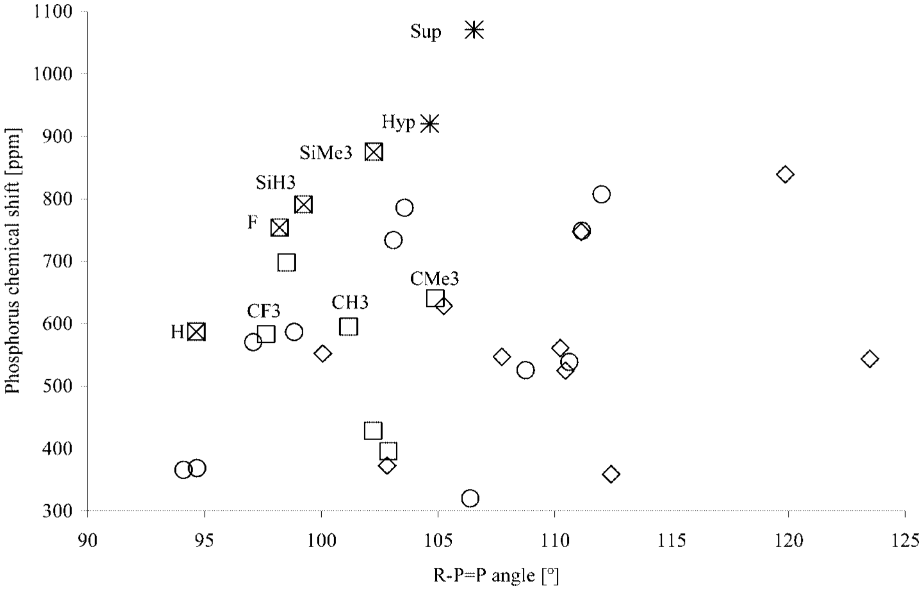

Figure 9. Relation between the R–P=P angle and chemical shifts of phosphorus at ab initio/NMR level DFT-A for *trans* (squares), *cis* (diamonds) and cyclic (circles) diphosphenes. A cross denotes the *trans*-disilylated molecules and the additional cross (forming an asterisk) marks the molecules that are known experimentally.

bond angles of *trans*-disilyldiphosphenes cause a large change of the phosphorus shift, which is different from the *trans* carbon analogues, as shown for the substituents H, CF_3, CH_3 and CMe_3. Here, a difference of the bond angles of more than 10° (see also Table 3) causes a shift change of no more than 50 ppm. As is to be expected, the P=P–R angle and the bulkiness of R correlate so that the shift also correlates with the calculated cone angles, which are 92.9°, 123.2°, 175.9° and 211.2° for SiH_3, $SiMe_3$, Hyp and Sup, respectively.

Remarkably, the chemical-shift changes for the *cis* isomers per unit angle change are much smaller. For the *cis* series with H, F, SiH_3 and $SiMe_3$, the calculated bond angles are 100.2°, 105.2°, 111.1° and 119.9°, with shift values of δ = 552, 628, 747 and 839 ppm, respectively, which gives a linear fit $\delta_{^{31}P} = -923 + 15\alpha$ (*cc* = 0.982). In the corresponding alkyl series H, CF_3, CH_3 and CMe_3, the shift is almost independent of the bond angle: all values are between δ = 525 and 552 ppm with bond angles between 100° and 123°. The shift values for *cis*- and *trans*-(H_2N)-P=P(NH_2) and -(Me_2N)P=P(NMe_2) do not fit into these correlations as they are much lower (between δ = 350 and 400 ppm). This is consistent with previous phosphorus NMR investigations that an increased electronegativity of the atom attached to the phosphorus atom causes an upfield shift.[21] In diphosphenes with P–C or P–Si bonds, β-alkylation, i.e. replacing CH_3 or SiH_3 by CH_2R and SiH_2R, always increases *α* as the cone angle of the substituent becomes larger and a downfield shift occurs. With the amino-substituted *cis*-diphosphenes $(H_2N)P{=}P(NH_2)$ and $(Me_2N)P{=}P(NMe_2)$ the opposite effect is observed; an upfield shift of about 20 ppm is predicted by the ab initio calculations.

The *cis*-E–P=P–E group in the cyclic compounds shows similar small effects of the bond angle on $\delta_{^{31}P}$. In agreement with a positive angle vs. shift correlation, $\delta_{^{31}P}$ of the six-membered rings increases compared to the corresponding five-membered rings.

All carbon-substituted diphosphenes are predicted to possess phosphorus resonances in the range between δ = 525 and 641 ppm, which does not overlap with the range for silyl-substituted diphosphenes [δ = 734 ppm for *cyclo*-1,2-diphospha-3,5-disilacyclopent-1-ene and δ = 875 ppm for *trans*-$(Me_3Si)P{=}P(SiMe_3)$]. Similarly, the amino-substituted diphosphenes show up with distinguishable chemical shifts in the range δ = 325–425 ppm, at higher field than the alkyldiphosphenes.

Conclusions

Along with the synthesis of the first example of a bis(oligosilyl)diphosphene, several synthetic refinements for the generation of phosphorus–phosphorus double bonds have been developed. The concentration-dependent product formation in the reaction of Hyp–PCl–$SiMe_3$ with KO*t*Bu indicates the intermediacy of a hypersilylphosphanylidene. The green colour of the diphosphene is in agreement with the weak n–π* absorption band at 632 nm obtained from DFT calculations. Geometries and GIAO/MP2 as well as GIAO/B3LYP chemical-shift calculations have been performed for the H-, SiH_3-, and $SiMe_3$-substituted parents of the experimentally investigated molecules. The relation (*cc* = 0.984; 16 examples with a P=P bond) between the large basis set MP2 and B3LYP/6-31G* results provide an equation [$\delta_P(\text{MP2-C}) = 0.84\times\delta_P(\text{B3LYP})$] with a negligible intercept. The correction factor has been successfully applied to the bare triphosphaallyl anion, resulting in differences of less than 32 ppm with respect to the NMR spectroscopic data of the complex of the anion with $K(THF)_n$ (**4**). The R–P=P bond angle vs. chemical shift relationship for 33 molecules with an –P=P– moiety has been analysed: *trans*-R–P=P–R shows larger shifts with larger angles (approximately 40 ppm per degree), although little effect is seen for *cis*-R–P=P–R (including endocyclic moieties), probably due to compensation resulting from geometric constraints. While previous model computations only considered R = H and SiH_3 (as placeholder for supersilyl) the present set expands the scope to $SiMe_3$ and, in special cases, to hypersilyl, $Si(SiMe_3)$. The change of geometric parameters from the SiH_3 to the $SiMe_3$ substituent is most obvious in *cis*-R–P=P–R, with a widening of the P=P–Si angle by 9°. In the other compounds considered this angle changes by only 2° (P_3-allyl) or 5° (cyclo-P_3). This is in agreement with NMR shifts of cyclotriphosphanes with R = H, Me, *i*Pr, and *t*Bu, which exemplify steric effects reflected in NMR signals.[22]

Experimental Section

General Remarks: All syntheses and manipulations were carried out under either N_2 or Ar using standard Schlenk techniques. Solvents were distilled from sodium, potassium, sodium/potassium alloy or $LiAlH_4$ prior to use. Elemental analyses were performed with a Heraeus Vario Elementar.

Ab Initio Calculations: The B3LYP/6-31+G* method was used for geometry optimisation, examining all stationary points by analytical frequency calculations with the Gaussian 98 program package.[23] For selected minimum geometries the magnetic shielding was calculated with the GIAO approach at the B3LYP/6-31G* and MP2 level with the basis sets 6-31G*, 6-311G* and 6-311+G**, and transformed into chemical shifts (see Table 3). The UV spectra were obtained by time-dependent DFT calculations with the hybrid B3LYP functional and 6-311+G(d) basis set.

Spectroscopy: NMR spectra were recorded with a Bruker MSL 300 or a Varian Unity Inova 300 spectrometer. The ^{29}Si and ^{31}P NMR spectra were measured for solutions in THF or toluene in 10-mm tubes with capillaries of D_2O serving as external lock. ^{31}P-^{31}P COSY spectra were recorded at 25 °C from a solution in C_6D_6 using 4096×4096 data points and a sweep width of 10582 Hz, The time required for an experiment was about 11 h. Raman spectra were recorded with a JobinYvon T64000 triple monochromator equipped with a CCD detector and a frequency-doubled Nd:YAG laser operating at 532 nm with a power of 10 mW. Samples were placed in 1-mm capillaries and sealed under dry, oxygen-free nitrogen. The UV/Vis spectrum of a solution of bis(hypersilyl)diphosphene in *n*-hexane was measured with a Perkin–Elmer Lamda 2S spectrometer in the range 200–700 nm.

X-ray Structure Analysis of 2: The crystal was mounted onto the tip of a glass fibre and data collection was performed with a Bruker-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The data was reduced to F_o^2 and corrected for absorption effects with SAINT[24] and SADABS,[25] respectively. The structure was solved by direct methods and refined by full-matrix least-squares methods (SHELXL-97).[26] All non-hydrogen atoms were refined with anisotropic displacement parameters and were located in positions calculated to correspond to standard bond lengths and angles. The diagrams were drawn with 30% probability thermal ellipsoids, with all hydrogen atoms omitted for clarity. Selected data are collected in Table 4. CCDC-291188 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of Bis(hypersilyl)diphosphene (2): Solid C_2Cl_6 (0.21 g, 0.87 mmol) was added to a solution of $HypP(SiMe_3)_2$ (0.31 g, 0.73 mmol) in 20 mL of toluene and the reaction mixture was stirred at room temperature overnight. The solvent and all volatile reaction products such as C_2Cl_4 and $ClSiMe_3$ were then carefully removed by concentration in vacuo. The oily residue of pure **1** was dissolved in 20 mL of THF and a solution of *t*BuOK (0.09 g, 0.76 mmol) in 10 mL of THF was added dropwise at –70 °C. The colour slowly changed to light-green. The mixture was stirred for another 2 h and then warmed to room temperature. The solvent

Table 4. Crystal data and structure refinement for bis(hypersilyl)-diphosphene.

Empirical formula	$C_{27}H_{81}P_3Si_{12}$
Formula mass	835.91
T [K]	100(2)
Wavelength [Å]	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	9.3084(19)
b [Å]	13.495(3)
c [Å]	23.693(5)
α [°]	94.59(3)
β [°]	100.94(3)
γ [°]	107.23(3)
V [Å^3]	2761.3(10)
Z	2
$\rho_{\text{calcd.}}$ [g cm^{-3}]	1.005
Absorption coefficient [mm^{-1}]	0.385
$F(000)$	912
Crystal size [mm]	0.45 × 0.28 × 0.16
θ range [°]	1.60–26.37
	$-11 < h < 11$
	$-16 < k < 16$
	$-29 < l < 29$
Reflections collected/unique	22108/11119 [R(int) = 0.0509]
Completeness to θ = 22.00°	98.4%
Absorption correction	SADABS
Refinement method	full-matrix least squares on F^2
Data/restraints/parameters	11119/0/406
Goodness-of-fit on F^2	1.006
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0593$, $wR_2 = 0.1346$
R indices (all data)	$R_1 = 0.0989$, $wR_2 = 0.1443$
Largest diff. peak/hole [e Å^{-3}]	0.524/–0.315

was removed by evaporation in vacuo and replaced with pentane. Light-green crystals of **2** (0.19 g, 95%) with a quality suitable for X-ray diffraction were obtained at –30 °C. $C_{18}H_{54}P_2Si_8$ (557.32): calcd. C 38.79, H 9.77; found C 37.90, H 9.52. ^{31}P NMR: δ = +735.0 ppm. ^{29}Si NMR: δ = –56.7 (pseudo-t, $|^1J_{P,Si} + {}^2J_{P,Si}|$ = 46.0 Hz), –9.9 (pseudo-t, $|^2J_{P,Si} + {}^3J_{P,Si}|$ = 7.1 Hz, SiMe$_3$) ppm.

Synthesis of Potassium hypersilyltriphosphenide (4): *t*BuOK (0.22 g, 1.96 mmol) was dissolved in 10 mL of THF and a solution of **1** (0.73 g, 1.88 mmol) in 20 mL of THF was added dropwise at –60 °C over a period of 30 min. The colour of the reaction mixture turned dark brown. After completion, the reaction mixture was warmed to room temperature, whereby the colour changed to deep violet. According to the ^{31}P NMR spectrum, **4** formed almost quantitatively (>95%) with traces of HypPH$_2$ (<5%) as a by-product. Attempts to crystallise **4** as the [18-crown-6·K]$^+$ salt failed. ^{31}P NMR: δ = +705.5 (t), +197.5 (d) ppm.

Reaction of Bis(hypersilyl)diphosphene with 2,3-Dimethylbutadiene. Formation of 5: Compound **2** (0.06 g, 0.11 mmol) was dissolved in 1 mL of THF and the solution was transferred into an NMR tube. 2,3-Dimethylbutadiene (0.073 g, 0.188 mmol) was then added. After 1 h at room temperature, the green colour had disappeared. According to the NMR spectra, the [4+2] cycloaddition product **5** had formed almost quantitatively (≥95%). No attempt to crystallise the compound was made. ^{31}P NMR: δ = –137.3 (s) ppm. ^{29}Si NMR: δ = –89.5 (pseudo-t, $|^1J_{P,Si} + {}^2J_{P,Si}|$ = 37.0 Hz), –9.8 (pseudo-t, $|^2J_{P,Si} + {}^3J_{P,Si}|$ = 10.6 Hz, SiMe$_3$) ppm.

Thermal Decomposition of Bis(hypersilyl)diphosphene. Formation of 6: Compound **2** (0.06 g, 0.11 mmol) was dissolved in 10 mL of toluene and refluxed for 4 h. After this period, the green colour had disappeared completely and the signal of **2** could no longer be detected in the ^{31}P NMR spectrum as **6** had formed almost quantitatively, along with some HypPH$_2$. Not unexpectedly, **6** also formed when **4** was treated with HypCl. Removal of the toluene by concentration in vacuo gave an oily residue, which turned out to be impossible to purify so no crystals could be grown, despite the use of different solvents. Attempts to purify **6** by sublimation failed due to decomposition, therefore no elemental analysis was carried out. ^{31}P NMR: δ = –233.0 (q), –241.3 (q), –260.9 (q) ppm. For a discussion of the spectra, see Synthesis section.

Supporting Information (see also the footnote on the first page of this article): Cartesian coordinates of the $(H_3Si)_3SiP{=}PSi(SiH_3)_3$ minima obtained by B3LYP/6-31+G(d) calculations with Gaussian98.

Acknowledgments

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