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Imino-Bridged Bisphosphaalkenes (2,4-Diphospha-3-azapentadienes)

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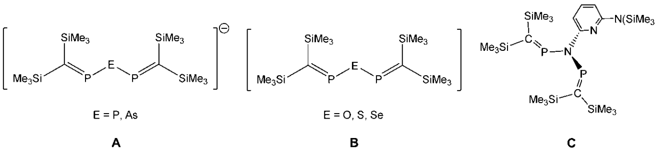
Abstract: Deprotonation of aminophosphaalkenes $(RMe_2Si)_2C{=}PN(H)(R')$ (R = Me, *i*Pr; R′ = *t*Bu, 1-adamantyl (1-Ada), 2,4,6-$tBu_3C_6H_2$ (Mes*)) followed by reactions of the corresponding Li salts $Li[(RMe_2Si)_2C{=}P(M)(R')]$ with one equivalent of the corresponding *P*-chlorophosphaalkenes $(RMe_2Si)_2C{=}PCl$ provides bisphosphaalkenes (2,4-diphospha-3-azapentadienes) $[(RMe_2Si)_2C{=}P]_2NR'$. The thermally unstable *tert*-butyliminobisphosphaalkene $[(Me_3Si)_2C{=}P]_2NtBu$ (**4a**) undergoes isomerisation reactions by Me_3Si-group migration that lead to mixtures of four-membered heterocyles, but in the presence of an excess amount of $(Me_3Si)_2C{=}PCl$, **4a** furnishes an azatriphosphabicyclohexene $C_3(SiMe_3)_5P_3NtBu$ (**5**) that gave red single crystals. Compound **5** contains a diphosphirane ring condensed with an azatriphospholene system that exhibits an endocylic P=C double bond and an exocyclic ylidic $P^{(+)}{-}C^{(-)}(SiMe_3)_2$ unit. Using the bulkier $iPrMe_2Si$ substituents at three-coordinated carbon leads to slightly enhanced thermal stability of 2,4-diphospha-3-azapentadienes $[(iPrMe_2Si)_2C{=}P]_2NR'$ (R′ = *t*Bu: **4b**; R′ = 1-Ada: **8**). According to a low-temperature crystal-structure determination, **8** adopts a non-planar structure with two distinctly differently oriented P=C sites, but ^{31}P NMR spectra in solution exhibit singlet signals. ^{31}P NMR spectra also reveal that bulky Mes* groups (Mes* = 2,4,6-$tBu_3C_6H_2$) at the central imino function lead to mixtures of symmetric and unsymmetric rotamers, thus implying hindered rotation around the P–N bonds in persistent compounds $[(RMe_2Si)_2C{=}P]_2NMes^*$ (**11a**, **11b**). DFT calculations for the parent molecule $[(H_3Si)_2C{=}P]_2NCH_3$ suggest that the non-planar distortion of compound **8** will have steric grounds.

Keywords: bisphosphaalkenes • density functional calculations • heterocycles • PNP ligands • X-ray diffraction

Introduction

Multiply unsaturated organophosphorus compounds are useful tools in coordination chemistry and catalysis, but as energy-rich compounds they are also excellent starting materials for cycloaddition reactions that lead to heterocyles, cages and polymers.[1,2] The 2,3,4-triphosphapentadienide anion $[(Me_3Si)_2C{=}P]_2P^-$ (Scheme 1A; E = P),[3] which allows electronic communication between the π systems (P=C bonds) of two neighbouring phosphaalkene moieties, is a precursor to P_3C_2 heterocycles and bicycles.[3] Its heavier 3-



Scheme 1. Heteroatom-bridged bisphosphaalkenes.

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arsenic congener $[(Me_3Si)_2C{=}P]_2As^-$ (Scheme 1A; E = As)[4] as well as isoelectronic uncharged species $[(Me_3Si)_2C{=}P]_2E$ (E = O, S, Se; Scheme 1B)[5,6] are also known, but nitrogen-bridged derivatives (2,4-diphospha-3-azapentadienes) are extremely rare. $[Ph(Me_3Si)C{=}P]_2N(nC_3H_7)$,[7] the single *N*-alkyl-2,4-diphospha-3-azapentadiene already reported in the literature, is thermally unstable, and only a particular 2-[6-bis(trimethylsilyl)amino]pyridylimino-bridged bisphosphaalkene (Scheme 1C), which contains its P=C functions orientated orthogonally out of the NP_2 plane, was found to be a stable compound.[8] Related 2,4-diphospha-1,3,5-triazapentadienes $(RN{=}P)_2NR'$, however, are well established.[9] In the last decade, bifunctional phosphaalkene ligands have led to remarkable applications in catalysis.[2,10,11] The recent observation that two-coordinated phosphorus atoms from "mono-unsaturated" *P*-(phosphanylamino)phosphaalkene ligands $(Me_3Si)_2C{=}P\text{-}N(R)\text{-}PPh_2$ tend to undergo carbene-like insertion reactions into Pd–Cl and Pt–Cl bonds that lead to unique metalla(chloro)ylid complexes[12] led us to a focus on stable "bi-unsaturated" iminobisphosphaalkenes that may also exhibit unusual behaviour as ligands in transition-metal chemistry, and, because of the inductively electron-withdrawing and π-conjugating properties of the central nitrogen atom,[13,14] offer particular tunable π-acceptor properties.

The first attempts to prepare compounds related to the unstable $[Ph(Me_3Si)C{=}P]_2N(nC_3H_7)$ according to Appel's protocol,[7] *P*-chlorophosphaalkene/primary amine, using $(Me_3Si)_2C{=}PCl$ (**1a**) in place of $Ph(Me_3Si)C{=}PCl$ as a starting material,[15] were unsuccessful, and aminophosphaalkenes $(Me_3Si)_2C{=}PNHR$ with bulkier substituents at nitrogen (R = *t*Bu, $SiMe_3$[13]) were unreactive under amine-liberation conditions.[16] Subsequently, we turned to alkali metal chloride elimination procedures based on the deprotonation of the aminophosphaalkene $(Me_3Si)_2C{=}PN(H)tBu$[13] followed by coupling of the in situ prepared anion $[(Me_3Si)_2C{=}PNtBu]^-$[16,17] with *P*-chlorophosphaalkene **1a**. Since the insufficient stability of the products precluded the isolation of single-crystalline solids, we chose bulkier silyl groups (*i*Pr-Me_2Si) at carbon for reactions of anions $[(RMe_2Si)_2C{=}PNR']^-$ with the related chlorophosphaalkenes $(RMe_2Si)_2C{=}PCl$ (**1**)[17–19] To improve crystallisation properties of thermolabile *N*-alkyl products, *N*-1-adamantyl derivatives were also introduced into our study. Additional experiments were carried out with *N*-Mes* derivatives (Mes* = 2,4,6-$tBu_3C_6H_2$).[14,16] Experimental results are described in the following.

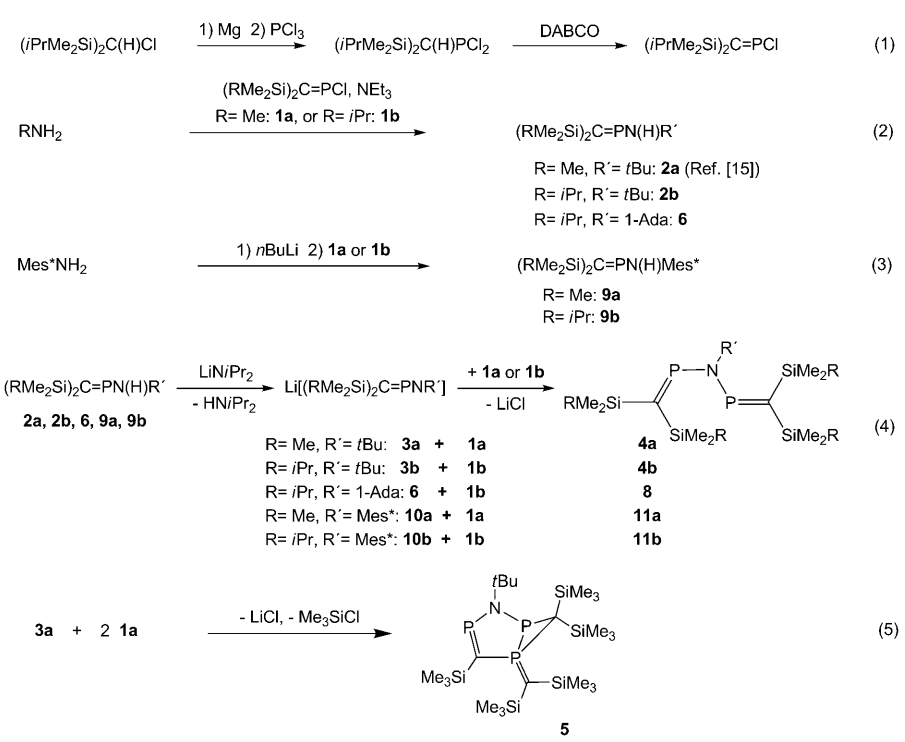
Results and Discussion

Syntheses, reactions and structures: The numbering of starting materials, their reactions and products is depicted in Scheme 2.

New alkyl- and arylaminophosphaalkenes: The pathway to the new chlorophosphaalkene **1b** and to new aminophosphaalkenes **2b**, **6**, **9a** and **9b** is described in Equations (1)–(3) (see Scheme 2).[5,16b,18,19]

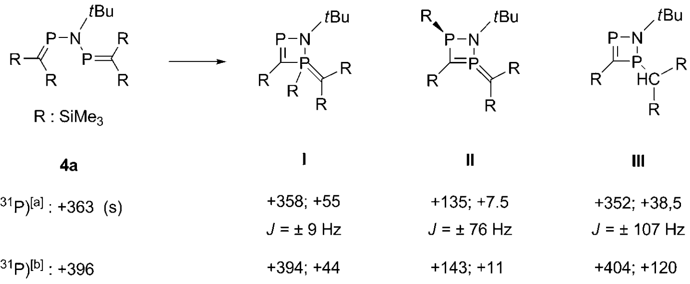
***t*Butylimino-bridged bisphosphaalkenes**: Lithium salts Li-$[(RMe_2Si)_2C{=}PN(tBu)]$ [**3a**: R = Me; **3b**: R = *i*Pr; Eq. (3)] were generated by deprotonation of the parent aminophosphaalkenes **2a**, **2b** with lithium diisopropylamide (LDA) in THF and subsequent removal of iPr_2NH in vacuo.

Compounds **3a** and **3b** react with the corresponding *P*-chlorophosphaalkenes[15,19] at temperatures below −40 °C in a straightforward manner to furnish solutions of the desired *tert*-butylimino-bridged bis-phosphaalkenes **4a**, **4b**, which exhibit singlet signals in ^{31}P NMR spectra. Raising the temperature to 0 °C and above leads to decomposition reactions, as indicated by the increasing intensity of one or more ^{31}P NMR spectroscopic signals that appear as AX-type (d,d) patterns.



Scheme 2. Numbering of starting materials, intermediates, and products DABCO = diazabicyclooctane.

In the case of $[(Me_3Si)_2C{=}P]_2N(tBu)$ (**4a**), one of the new AX patterns (^{31}P NMR: $\delta = 358.4$, 55.1 ppm, $J = 9$ Hz; species **I**) indicates the presence of a phosphaalkene-type ^{31}P nucleus coupling with a tri- or tetra-coordinated phosphorus atom. The second AX pattern (^{31}P NMR: $\delta = 135$, 7.5 ppm, $J = 76$ Hz; species **II**) involves two nuclei that do not belong to phosphaalkene functions. In some cases, apparently favoured by protic impurities, a third AX pattern appears (^{31}P NMR: $\delta = 351.9$, 38.5 ppm, $J = 107$ Hz; species **III**) that has to be assigned to another $^{31}P({=}C)$ nucleus coupling with another tri- or tetra-coordinated phosphorus atom that is part of a ^{31}P-C-H function ($^2J(P,H) = 13$ Hz). Possible structures with the measured and computed (see below) ^{31}P NMR spectroscopic chemical shifts are depicted in Scheme 3. The calculated and measured values are in qualitative agreement (see also the Supporting Information).



Scheme 3. Proposed structures of products from decomposition of **4a**. [a] Measured and [b] calculated at the B3LYP/cc-pVTZ//B3LYP/6-31+G* level of theory (in ppm).

The addition of **1a** to a reaction mixture containing decomposing **4a** leads to consumption of **4a** and of rearranged species **I**, with formation of a new compound **5** that exhibits an AMX pattern in the ^{31}P NMR spectrum (^{31}P NMR: $\delta =$ 331.2, −17.2, −24.0 ppm), involving one $^{31}P{=}C$ phosphorus atom coupling with two inequivalent "*non*-(P=C)" ^{31}P nuclei in a diphosphirane unit. B3LYP/cc-pVTZ//B3LYP/6-31+G* gauge-including atomic orbital (GIAO) calculations predict chemical shifts of $\delta = 356.9$, −35.3 and −4.5 ppm for the σ^2,λ^3, σ^3,λ^3 and σ^4,λ^5-phosphorus, respectively (for further calculations, see the Supporting Information). Compound **5** is also sometimes observed as a trace impurity in the course of 1:1 reactions of **1a** with **3a**, and it can be isolated from the straightforward 2:1 reaction in fair crude yield [Eq. (5)]. An X-ray crystal-structure determination reveals that **5** is a 5-methylene-2-aza-1,3,5-triphosphabicyclo[3.1.0]hex-2-ene that contains an endocyclic P=C bond (1.679(3) Å) "in conjugation" with an exocyclic ylidic $P^{(+)}{-}C^{(-)}(SiMe_3)_2$ function (1.688(3) Å) involving one of the two bridgehead phosphorus atoms that are part of a diphosphirane together with another $C(SiMe_3)_2$ group (see Scheme 2, Figure 1).

Steric crowding around the quaternary carbon atom C8, including repulsion between the two $C(SiMe_3)_2$ groups bridged by P1, correlates with exceptionally long bond lengths for C8−Si3, C8−Si4 and C8−P2 (all >1.9 Å).

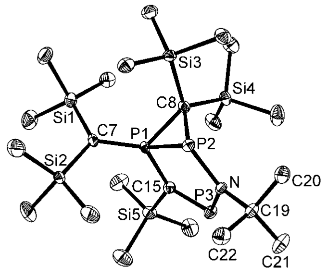
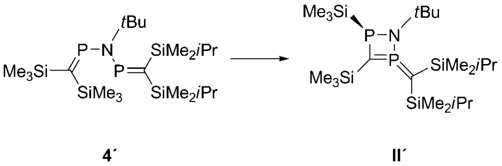


Figure 1. Molecular structure of **5**. Selected bond lengths [Å] and angle [°]: P1−P2 2.1933(13), P1−C7 1.688(3), P1−C15 1.783(3), P1−C8 1.829(3), P2−C8 1.915(3), P2−N 1.720(3), P3−N 1.694(3), P3−C15 1.679(3); P2-N-P3 120.71(16). Hydrogen atoms are omitted for clarity. Atoms are drawn as 50% thermal ellipsoids.

We assume that the motif of a (p–p)π P=C double bond "in conjugation" with an exocyclic ylidic $P^{(+)}{-}C^{(-)}$ from compound **5** is also present in species **I** (Scheme 3), which is a likely precursor to **5** (see below).

Compound **5** is derived from **1a** by reaction with **4a** or with species **I** (Scheme 3) by elimination of one equivalent of Me_3SiCl. The formation of rearranged products **I** and **II** from **4a** involves trimethylsilyl-group migration, and **III** is apparently a product of protolytic P−Si bond cleavage, followed by proton migration to the basic ylid carbon atom.

When in a "cross" experiment anion **3a** reacted in an NMR spectroscopy tube with the bulkier chlorophosphane **1b**, or anion **3b** reacted with **1a**, the mixed-substituted bisphosphaalkene $(Me_3Si)_2C{=}P{-}N(tBu){-}P{=}C(SiMe_2iPr)_2$ (AB pattern, ^{31}P NMR: $\delta = 365.3$, 361.8 ppm, $^2J(P,P) = \pm 18$ Hz) was accompanied by only one rearranged species **II′** (AX pattern, ^{31}P NMR: $\delta = 136.7$, 7.3 ppm, $J = 78$ Hz) related to the proposed species **II** from the "symmetric" experiment. We conclude that one of the silyl-group migration pathways (exocyclic ylid function) is closed when two bulkier $iPrMe_2Si$ groups are introduced at the carbon atom of one of the P=C bonds (Schemes 3 and 4).



Scheme 4. Proposed structure of a major product from the cyclisation of the unsymmetric bisphosphaalkene $(Me_3Si)_2C{=}P{-}N(tBu){-}P{=}C(SiMe_2iPr)_2$.

In the case of *tert*-butyliminobisphosphaalkene **4b** (with only $iPrMe_2Si$ groups at carbon), decomposition is significantly slower than that in the case of **4a**, but isolation of pure **4b** was precluded by decomposition (see the Experimental Section). Subsequently, single crystals could be obtained at low temperatures by switching to the corresponding *N*-1-adamantyliminophosphaalkene anion **7**, thereby furnishing *N*-1-adamantyliminobis-phosphaalkene **8**, which was subjected to X-ray structure determination as a tetrahydrofuran solvate. In solution, **8** exhibits a ^{31}P NMR spectroscopic singlet resonance signal, but in the solid the two P=C moieties of each independent molecule are inequivalent (Figure 2, top). The three independent molecules in solid **8** (Figure 2. bottom) exhibit different adamantyl-group orientations relative to the common "helically distorted" CPNPC skeleton and undergo different contacts to the solvating THF molecules. The conformations of the non-planar C-P1-N(R)-P′-C′ backbones (in molecule #1: torsion angles C11-P1-N-P2 and C22-P2-N-P1) of the three independent molecules are similar (molecule #1: −40.9(2) and −55.6(2)°; molecule #2: −41.1(2) and −54.2(2)°; molecule #3: −48.4(2) and −48.5(2)°), with the P=C moieties being directed out of the NP_2 planes about halfway between orthogonal[8] and planar. Within the non-planar CPNPC moieties, P=C (166.4–167.0 Å) and P−N bonds (171.2–173.7 Å) appear essentially undisturbed by conjugative effects. In this respect, **8** is comparable to the 2-[6-bis(trimethylsilyl)amino]pyridylimino-bridged bisphosphaalkene C (Scheme 1).[8] The latter compound, which exhibits a ^{31}P NMR spectroscopic AM pattern in solution at −60 °C, shows sterically hindered PN bond rotation at this temperature, but equilibration of the two phosphorus nuclei on the ^{31}P NMR spectroscopic time scale occurs at room temperature.[8]

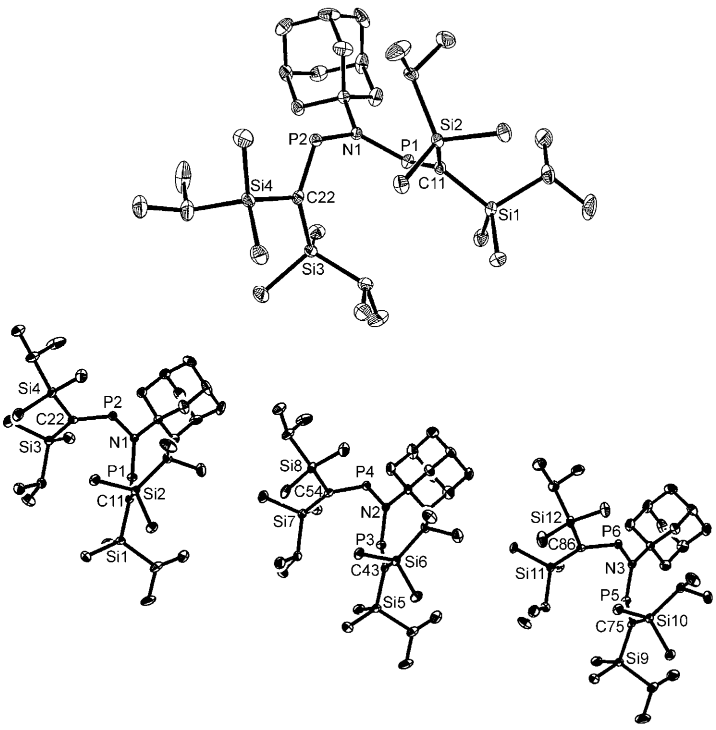
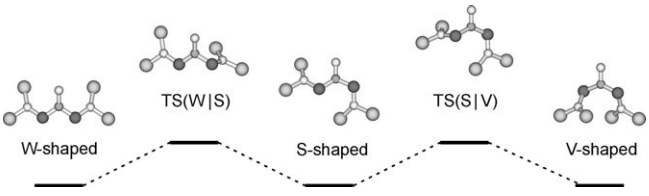


Figure 2. Top) Molecular structure of **8**, molecule #1. Selected bond lengths [Å] and angles [°]: P1−C11 1.6670(3), P2−C22 1.6606(3), P1−N 1.712(2), P2−N 1.737(2), C23−N 1.524(13); P1-N-P2 126.77(13). P1-N-C23 119.36(18), P2-N-C23 113.72(17), C11-P1-N-P2 −40.9(2), C22-P2-N-P1 55.6(2). Hydrogen atoms are omitted for clarity. Atoms are drawn as 50 % thermal ellipsoids. Bottom) Arrangement of the three independent molecules of **8**.

^{31}P NMR spectroscopic study on N-Mes*-bridged bisphosphaalkenes: The reaction mixtures from metalation of **9a** or **9b** with LDA, followed by reactions of **10a** with **1a** and of **10b** with **1b**, each exhibit in the ^{31}P NMR spectrum a singlet signal accompanied by an AM pattern (**11a**: $\delta = 352$ (s), 329 (d), 323 ppm (d), $^{2}J(P,P) = 7.4$ Hz; **11b**: $\delta = 352$ (s), 332 (d), 326 ppm (d), ^{2}J (P,P) = 13.5 Hz), and another small singlet assignable to $[(Me_3Si)_2C{=}P]_2O$ ($\delta = 353$ ppm) and $[(i\text{Pr}Me_2Si)_2C{=}P]_2O$ ($\delta = 354$ ppm).[5,18] Clearly, the bulky NMes* groups enhance the rotational barrier(s) of rotameric interconversion of symmetric *sym*-**11a** or *sym*-**11b** and unsymmetric S-shaped *asym*-**11a** or *asym*-**11b**. Initially, the ^{31}P NMR spectroscopic peak height of symmetric *sym*-**11b** is larger than the total intensities of the AM pattern from *asym*-**11b** (ratio of about 5:2), but after a slight relative increase of the amount of asymmetric species within two days, an approximately 5:3 ratio of the two species in solution remains unchanged for an extended period. Enrichment of one of these species from the oily crude products was not achieved.

DFT calculations on 2,4-diphospha-3-azapentadienes (iminobisphosphaalkenes): First we explored the potential-energy surface of the parent $[(H_3Si)_2C{=}P]_2NCH_3$ system by optimising the S-shaped, W-shaped and V-shaped C=P−N−P=C moieties (Scheme 5).



Scheme 5. $[(H_3Si)_2C{=}P]_2NCH_3$ rotamers and their connecting transition structures.

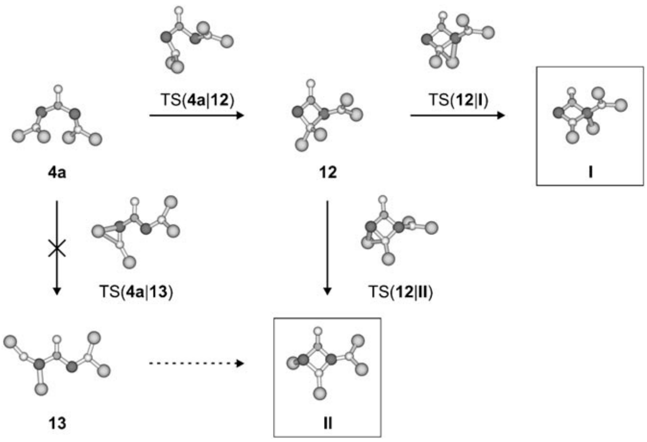
Whereas for the parent iminobisphosphaalkene $[(H_3Si)_2C{=}P]_2NCH_3$ a small activation barrier and energetically close-lying rotamers were obtained at each investigated level of the theory (Table 1), with bulkier groups no W-shaped rotamers could be found on the B3LYP/6-31+G* potential-energy hypersurface, and the energy difference between the S- and V-shaped rotamers is much larger than in the case of the parent molecule. In the case of $[(Me_3Si)_2C{=}P]_2NMes^*$, the unsymmetric S-shaped form is more stable by 8–9 kcal mol^{-1} than the quasi-symmetric V-shaped form at different levels of theory (see the Supporting Information). Clearly, the large Mes* substituent hinders the rotation of the phosphaalkene units, and both the V- and S-shaped rotamers can be present in solution, in good agreement with the ^{31}P NMR spectroscopic investigations. For the compounds $[(Me_3Si)_2C{=}P]_2NR$ with R = 1-Ada and *t*Bu, neither S- nor W-shaped rotamers form, but the quasi-symmetric V-shaped rotamer (in agreement with the X-ray struc-

Table 1. Relative energies (in kcal mol^{-1}) of the $[(H_3Si)_2C{=}P]_2NCH_3$ rotamers and activation barriers at different levels of theory on geometries obtained at the B3LYP/6-311+G** level.

	W-shaped	TS(W|S)	S-shaped	TS(S|V)	V-shaped
B3LYP/6-31+G*	0.5	3.8	0.0	3.6	2.3
B3LYP/6-311+G**	0.4	3.5	0.0	3.5	2.2
MPW1K/6-311+G**	0.5	3.8	0.0	3.7	2.1
MP2/6-311+G**	1.0	3.4	0.3	3.3	0.0

ture) was found, thereby providing (as observed) a singlet signal in the ^{31}P NMR spectra.

To understand the formation of four-membered-ring intermediates (**I**–**III**, Scheme 3) and thus the silyl-group migration, the reaction (Scheme 6) was calculated for model compounds. The bulky $SiMe_3$ and *t*Bu groups have a significant effect on the relative energies of the intermediates and transition structures (data for the smallest model systems with SiH_3/CH_3 groups are given in the Supporting Information for comparison). From **4a** a four-membered intermediate (**12**) can directly be obtained. Both observed decomposition products (**I** and **II**) can be formed from **12** by 1,2-shifts. Intermediate **13**, which can be converted to intermediate **II**, was also considered; its high energy (Table 2), however, excludes the possibility of this reaction pathway.



Scheme 6. Cyclisation pathway of alkyliminobisphosphaalkene $[(Me_3Si)_2C{=}P]_2N\mathit{t}Bu$ (methyl groups omitted for clarity).

The formation of the energy-rich four-membered-ring intermediate **12** is kinetically feasible (16–22 kcal mol^{-1} activation barriers at different levels), and from this species the more stable products **I** and **II** can be formed by means of reasonably small activation barriers, which are predicted to be significantly lower at MP2 than at the B3LYP level. It is worth noting that the stabilities of compounds **I** and **II** are comparable; furthermore, the activation barriers to them are also very similar. Thus the formation of both isomers is feasible, which is in good agreement with their experimental observation. To investigate the formation of **5** from **I** and chlorophosphaalkene $(Me_3Si)_2C{=}PCl$ (**3a**), the reactions shown in Scheme 7 were calculated. It is important to note that several attempts were made to explore possible transition structures (attack of **3a** from different directions), however, only **TS(I|14)**, which corresponds to an insertion into the σ^4,λ^5-P–N bond of **I** (Scheme 7), turned out to be a first-order saddle point. Intermediate **14**, which is formed from **TS(I|14)** according to intrinsic reaction coordinate (IRC) calculations, can be stabilised (Table 3) by Me_3SiCl elimination that leads to **15**. To check the reliability of the results, further calculations were carried out using the MPW1K functional as well as the MP2 method. Since for the SiH_3-substituted systems the relative energies obtained from single-point calculations at the B3LYP-optimised geometries differ only slightly from the values obtained at their optimised structures (see the Supporting Information), for the $SiMe_3$-substituted systems we have used the energies obtained from single-point calculations (Table 3). The wavefunctions of intermediates **14** and **15** and transition structures **TS(I|14)** and **TS(14|15)** are stable at the DFT levels, however, the Hartree–Fock wavefunction shows unrestricted Hartree–Fock (UHF) instability. Accordingly, the perturbation treatment of the unstable wavefunction can be in significant and unpredictable error, thereby rendering the corresponding Møller–Plesset second-order perturbation theory (MP2) results dubious. Apparently, for a highly accurate description of the electronic structure of **14** and **15**, multireference methods would be the best choice; unfortunately, the size of the investigated system excludes this possibility. Bicycle **5**, however, can properly be described by the closed-shell determinant at each level and it is far more stable (considering the energy of $SiMe_3Cl$) than the starting materials. (It should be noted that at the B3LYP/6-31+G* level **15** is somewhat more stable than **5**, which is in contrast with the observed formation of **5**. Using a larger basis set, the energy difference is reduced, whereas with the MPW1K functional and at the MP2/6-31+G* level, **5** is the thermodynamical sink in agreement with the experimental results. Nevertheless, the B3LYP/6-31+G*-optimised structure of **5** (see the Supporting Information) is similar to that obtained from the X-ray investigation.

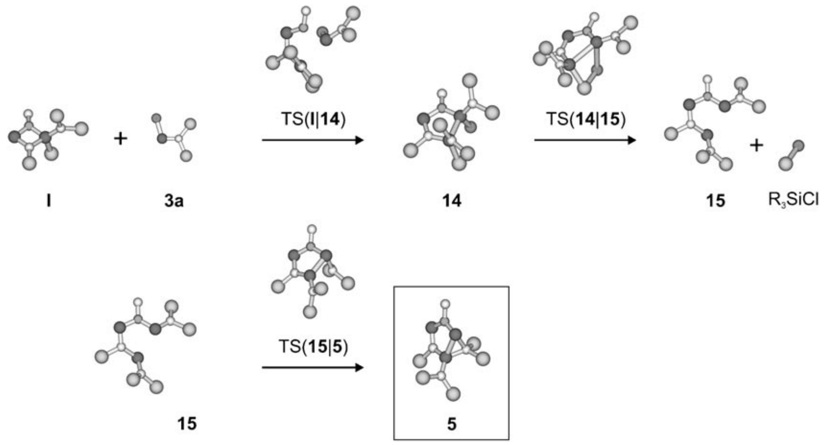
Table 2. Relative energies and activation barriers (compared to **4a**) for the $[(Me_3Si)_2C{=}P]_2N\mathit{t}Bu$ system at different levels of theory on geometries obtained at the B3LYP/6-31+G* level.

	4a	TS(**4a**|**12**)	**12**	TS(**12**|**I**)	**I**	TS(**12**|**II**)	**II**	TS(**4a**|**13**)	**13**
B3LYP/6-31+G*	0.0	21.5	14.9	29.4	6.0	29.6	5.6	47.0	35.4
B3LYP/6-311+G**	0.0	20.9	15.4	30.2	7.2	30.4	6.5	47.7	36.5
MPW1K/6-311+G**	0.0	19.6	10.7	23.1	−0.7	24.8	−0.1	50.6	38.4
MP2/6-31+G*	0.0	16.9	5.3	18.4	5.3	19.4	6.1	56.3	41.3

Table 3. Relative energies of transition structures (TS) and intermediates for the formation of azatriphosphabicyclohexene **5** from **I** and $(Me_3Si)_2C{=}PCl$ at different levels of theory on geometries obtained at the B3LYP/6-31+G* level.

	I+$(Me_3Si)_2C{=}PCl$	**TS (I|14)**	**14**	**TS (14|15)**	**15**+Me_3SiCl	**TS(15|5)**+Me_3SiCl	**5**+Me_3SiCl
B3LYP/6-31+G*	0.0	32.9	26.1	34.9	−21.6	1.7	−19.3
B3LYP/6-311+G**	0.0	32.0	25.4	34.1	−19.8	2.1	−19.3
MPW1K/6-311+G**	0.0	31.9	17.3	35.5	−14.3	−0.8	−30.8
MP2/6-31+G*	0.0	(0.4)[a]	(−14.2)[a]	(3.1)[a]	(−28.2)[a]	−17.8	−49.0

[a] The HF wavefunction showed UHF instability; the perturbation treatment is likely to be in significant error.



Scheme 7. Probable formation of bicyclic product **5** from the four-membered-ring **I** and phosphaalkene $(Me_3Si)_2C{=}PCl$ (**3a**) (methyl groups omitted for clarity).

Conclusion

tert-Butyliminobisphosphaalkenes $[(RMe_2Si)_2C{=}P]_2NtBu$ (**4a, 4b**; R = Me, *i*Pr), synthetically available from 1:1 reactions of *N*-metalated *P*-alkylaminophosphaalkenes with *P*-chlorophosphaalkenes, tend to isomerise by cyclisation with silyl-group migration. Related rearrangements explain the formation of an azatriphosphabicyclohexene $tBuNC_3P_3(SiMe_3)_5$ (**5**) from the reaction of $Li[(Me_3Si)_2C{=}PNtBu]$ with two equivalents of $(Me_3Si)_2C{=}PCl$. *C*-Isopropyldimethylsilyl groups slow down silyl migration reactions, allowing the low-temperature crystal-structure determination of $[(iPrMe_2Si)_2C{=}P]_2N(1\text{-Ada})$ (**8**), which exists in a helically distorted S-shaped conformation. ^{31}P NMR spectra reveal that, in solution, the ^{31}P nuclei of the P=C functions of **8** are equivalent (rapid interconversion of rotamers on the NMR spectroscopic timescale), whereas mixtures of rotamers are observed in solutions of iminobisphosphaalkenes with extremely bulky $(2,4,6\text{-}tBu_3C_6H_2)$ *N*-aryl groups. DFT calculations on less strained iminobisphosphaalkenes suggest that the non-planar configuration of compound **8** will have steric grounds and provide a likely mechanistic explanation for rearrangements by silyl-group migration.

Experimental Section

General methods: All experiments were carried out under oxygen-free nitrogen by using standard Schlenk techniques. NMR spectra were recorded using Bruker AC 200, Avance 200, Avance 400 and AMX 300 spectrometers, with 85 % H_3PO_4 and $SiMe_4$ as external or internal standards.

Aminophosphaalkenes

*$(iPrMe_2Si)_2C{=}PN(tBu)H$ (**2b**)*: *tert*-Butylamine (1.30 g, 17.86 mmol) was added dropwise to a solution that contained **1b** (5.02 g, 17.86 mmol), triethylamine (2.58 mL, 18.56 mmol) and pentane (100 mL) at −40 °C. The mixture was allowed to warm up slowly to room temperature and stirring was continued for 12 h. After removal of the solid triethylammonium salt and the solvent, vacuum distillation furnished at 70 °C (0.2 mbar) **2b** as a yellow oil (4.30 g, 76 %). ^1H NMR (300.1 MHz, C_6D_6, 25 °C): $\delta = 5.01$ (d, $^2J(H,P) = 12.34$ Hz, 1H; N*H*), 0.93 (d, $^4J(H,P) = 1.35$ Hz, 1H; C*H*$(CH_3)_2$), 0.86–0.83 (m, 13H; C*H*$(CH_3)_2$), 0.82 (s, 9H; $NC(CH_3)_3$), 0.08 (d, $^4J(H,P) = 3$ Hz, 6H; CH_3), 0.0 ppm (s, 6H; $SiCH_3$); ^{13}C NMR (75.4 MHz, C_6D_6, 25 °C): $\delta = 122.63$ (d, $^2J(C,P) = 71.8$ Hz; *C*=P), 52.88 (d, $^3J(C,P) = 9.8$ Hz; N*C*$(CH_3)_3$), 32.32 (d, $^3J(C,P) = 8.2$ Hz; $NC(CH_3)_3$), 18.36 (s; $CH(CH_3)_2$), 18.22 (d, $^4J(C,P) = 1.7$ Hz; $CH(CH_3)_2$), 16.30 (d, $^3J(C,P) = 3.0$ Hz; *C*H$(CH_3)_2$), 15.37 (d, $^3J(C,P) = 8.0$ Hz; *C*H$(CH_3)_2$), −1.01 (d, $^3J(C,P) = 1.68$ Hz; CH_3), −1.26 ppm (s; CH_3); ^{29}Si NMR (59.6 MHz, C_6D_6, 25 °C): $\delta = 2.03$ (d, $^2J(Si,P) = 38.8$ Hz), −4.17 ppm (d, $^2J(Si,P) = 8.7$ Hz); ^{31}P NMR (121.5 MHz, C_6D_6, 25 °C): $\delta = 310.26$ ppm; MS (EI): *m/z*: 317 $[M^+]$; elemental analysis calcd (%) for $C_{15}H_{36}NPSi_2$ (317.60): C 56.73, H 11.43, N 4.41; found C 56.24, H 12.15, N 4.22.

*$(iPrMe_2Si)_2C{=}PN(1\text{-}Ada)H$ (**6**)*: Compound **1b** (2.93 g, 10.4 mmol) was added dropwise to a solution that contained adamantylamine (1.58 g, 10.4 mmol) and triethylamine (2.2 mL, 21.0 mmol) and pentane (50 mL) at −40 °C. The reaction mixture was allowed to warm up slowly to room temperature and the stirring was continued for 12 h. The solid triethylammonium salt was removed by filtration and after removal of the solvent in vacuo **6** was isolated as a white solid (3.8 g, 92 %). M.p. 48–49 °C. ^1H NMR (300.1 MHz, C_6D_6, 25 °C): $\delta = 4.96$ (d, $^2J(H,P) = 12.5$ Hz, 1H; N*H*), 1.73 (s, 3H; C*H*-Ada), 1.48 (d, $^4J(H,P) = 2.63$ Hz, 6H; CH_2-Ada), 1.26–1.37 (m, 6H; CH_2-Ada), 0.73–0.83 (m, 14H; C*H*$(CH_3)_2$), 0.01 (d, $^4J(H,P) = 2.76$ Hz, 6H; CH_3), 0.0 ppm (s, 6H; CH_3); ^{13}C NMR (75.4 MHz, C_6D_6, 25 °C): $\delta = 121.48$ (d, $^1J(C,P) = 72.04$ Hz; *C*=P), 52.92 (d, $^2J(C,P) = 8.75$ Hz; *C*-Ada), 43.13 (d, $^3J(C,P) = 8.1$ Hz; CH_2-Ada), 36.17 (s; CH_2-Ada), 29.95 (s; *C*H-Ada), 18.24 (s; $CH(CH_3)_2$), 18.02 (s; $CH(CH_3)_2$), 16.01 (d, $^3J(C,P) = 2.7$ Hz; *C*H$(CH_3)_2$), 15.08 (d, $^3J(C,P) = 8$ Hz; *C*H$(CH_3)_2$), −1.22 (d, $^3J(C,P) = 2.54$ Hz; CH_3), −1.39 ppm (d, $^3J(C,P) = 18$ Hz; CH_3); ^{29}Si NMR (59.6 MHz, C_6D_6, 25 °C): $\delta = 1.86$ (d, $^2J(Si,P) = 39.13$ Hz), −4.49 ppm (d, $^2J(Si,P) = 8.43$ Hz); ^{31}P NMR (121.5 MHz, C_6D_6, 25 °C): $\delta = 308.39$ ppm; MS (EI): *m/z* (%): 395 (8) $[M^+]$, 352 (30) $[M{-}iPr^+]$, 236 (45) $[M{-}iPr_2Me_3Si]^+$, 208 (100) $[M{-}iPr_2Me_3Si_2]^+$; elemental analysis calcd (%) for $C_{21}H_{42}NPSi_2$ (395.71): C 63.74, H 10.70, N 3.54; found: C 62.89, H 11.04, N 3.48.

*$(Me_3Si)_2C{=}PN(Mes^*)H$ (**9a**)*: A solution of 2,4,6-tri-*tert*-butylaniline (1.35 g, 5.15 mmol) in tetrahydrofuran (10 mL) was cooled at −40 °C

under a nitrogen atmosphere. *n*BuLi (2.1 mL of a 2.5 M hexane solution, 5.15 mmol) was slowly added to the stirred solution and the reaction mixture was warmed to room temperature with magnetic stirring over 1 h. The suspension was added dropwise to a solution of **1a** formed of $(Me_3Si)_2C{=}PCl$ (1.16 g, 5.15 mmol) in THF (15 mL) at −40 °C. Precipitation of the lithium salt with pentane, removal of the salt by filtration and removal of the solvent in vacuo gave **9a** as a yellow solid (2.15 g, 93 %). ^{1}H NMR (200 MHz, C_6D_6, 25 °C): $\delta = 7.25$ (br s, 2H; Ph), 6.13 (d, ^{2}J(H,P) = 9.2 Hz, 1H; N*H*), 1.29 (br s, 9H; *o*-*t*Bu), 1.06 (br s, 9H; *p*-*t*Bu), 0.15 (br s, 9H; C*H*$_3$), 0.07 ppm (d, ^{4}J(H,P) = 2.3 Hz, 9H; C*H*$_3$); ^{13}C NMR (50.32 MHz, C_6D_6, 25 °C): $\delta = 149.06$ (d, ^{2}J(C,P) = 2.6 Hz; *C*-*ipso*-Ph), 148.03 (d, ^{5}J(C,P) = 1.2 Hz; *C*-*p*-Ph), 140.29 (d, ^{1}J(C,P) = 108.1 Hz; *C*=P), 137.34 (d, ^{3}J(C,P) = 13.9 Hz; *C*-*o*-Ph), 123.24 (s; *C*-*m*-Ph), 36.87 (br s; *o*-*C*(CH_3)$_3$), 35.10 (br s; *p*-*C*(CH_3)$_3$), 33.72 (d, ^{5}J(C,P) = 4.2 Hz; *o*-C(*C*H$_3$)$_3$), 31.04 (s; *p*-C(*C*H$_3$)$_3$), 4.01 (d, ^{3}J(C,P) = 2.3 Hz; *C*H$_3$), 3.62 ppm (d, ^{3}J(C,P) = 15.0 Hz; *C*H$_3$); ^{31}P NMR (81.02 MHz, C_6D_6, 25 °C): $\delta = 318.1$ ppm.

(iPrMe$_2$Si)$_2$C=PN(Mes)H* (**9b**): A solution of 2,4,6-tri-*tert*-butylaniline (1.32 g, 5.03 mmol) in tetrahydrofuran (10 mL) was cooled at −40 °C under a nitrogen atmosphere. *n*BuLi (2.02 mL of a 2.5 M hexane solution, 1 equiv) was slowly added to the stirred solution and the reaction mixture was warmed to room temperature with magnetic stirring over 1 h. The suspension was added dropwise to a solution of **1b** formed from $(iPrMe_2Si)_2C{=}PCl$ (1.42 g, 5.03 mmol) in THF (15 mL) at −40 °C. Precipitation of the lithium salt with pentane, its removal by filtration and the removal of the solvent in vacuo gave **9b** as a cherry-red solid (2.16 g, 85 %). Single crystals suitable for X-ray analyses were obtained from hexane. M.p. 97–98 °C; ^{1}H NMR (300.1 MHz, C_6D_6, 25 °C): $\delta = 7.36$ (s, 2H; Ph), 6.37 (d, ^{2}J(H,P) = 9 Hz, 1H; N*H*), 1.47 (s, 9H; *o*-*t*Bu), 1.32 (d, ^{4}J(H,P) = 8 Hz, 1H; C*H*(CH_3)$_2$), 1.22 (s, 9H; *p*-*t*Bu), 1.01–1.05 (m, 13H; CH(C*H*$_3$)$_2$), 0.28 (s, 6H; C*H*$_3$), 0.21 ppm (d, ^{4}J(H,P) = 3 Hz, 6H; C*H*$_3$); ^{13}C NMR (75.4 MHz, C_6D_6, 25 °C): $\delta = 148.78$ (d, ^{2}J(C,P) = 2.8 Hz; *C*-*ipso*-Ph), 147.76 (s; *C*-*p*-Ph), 137.24 (d, ^{3}J(C,P) = 14.3 Hz; *C*-*o*-Ph), 123.95 (d, ^{1}J(C,P) = 76 Hz; *C*=P), 123.02 (s; *C*-*m*-Ph), 36.54 (s; *o*-*C*(CH_3)$_3$), 34.69 (s; *p*-*C*(CH_3)$_3$), 33.19 (d, ^{5}J(C,P) = 4 Hz; *o*-C(*C*H$_3$)$_3$), 31.32 (s; *p*-C(*C*H$_3$)$_3$), 17.92 (s; CH(*C*H$_3$)$_2$), 17.86 (d, ^{4}J(C,P) = 1.6 Hz; CH(*C*H$_3$)$_2$), 15.39 (d, ^{3}J(C,P) = 2.3 Hz; *C*H(CH_3)$_2$), 15.25 (s; *C*H(CH_3)$_2$), −0.87 (d, ^{3}J(C,P) = 2.5 Hz; *C*H$_3$), −1.06 ppm (d, ^{3}J(C,P) = 18.3 Hz; *C*H$_3$); ^{29}Si NMR (59.6 MHz, C_6D_6, 25 °C): $\delta = 2.1$ (d, ^{2}J(Si,P) = 38.6 Hz), −3.95 ppm (d, ^{2}J(Si,P) = 9.86 Hz); ^{31}P NMR (121.5 MHz, C_6D_6, 25 °C): $\delta = 325.0$ ppm; MS (EI): *m*/*z* (%): 505 (16) [*M*]$^+$, 406 (98) [*M*−*t*Bu*i*Pr+H]$^+$, 318 (11) [*M*−*t*Bu$_3$Me−H]$^+$, 290 (31) [*M*−(SiMe$_2$*i*Pr)$_2$C−H]$^+$, 246 (42) [M−NMes*]$^+$; elemental analysis calcd (%) for $C_{29}H_{56}NPSi_2$ (505.91): C 68.85, H 11.16, N 2.77; found: C 67.59, H 11.09, N 2.71.

Reactions of metalated aminophosphaalkenes with *P*-chlorophosphaalkenes

[(Me$_3$Si)$_2$C=P]$_2$NtBu (**4a**): LDA (1 mL of a 2 M THF/heptane/ethylbenzene solution, 1 equiv) was added to a solution of **2a** (0.5 g, 2 mmol) in diethyl ether (30 mL) at −40 °C under a nitrogen atmosphere. The mixture was warmed to room temperature and stirred for 12 h. ^{31}P NMR spectroscopic analysis of the solution showed quantitative formation of **3a** (^{31}P NMR (81 MHz, C_6D_6): $\delta = 425.5$ ppm). The formed *i*Pr$_2$NH and the solvent were removed in vacuo and the residue was dissolved in diethyl ether (30 mL). Compound **1a** (0.45 g, 2 mmol) was added slowly to this solution at −40 °C. The cooling bath was removed and the reaction mixture was allowed to warm slowly to room temperature. After 12 h, the lithium salt was removed by filtration and the solution was concentrated in vacuo followed by ^{31}P NMR spectroscopic analysis (81 MHz, C_6D_6): the singlet signal assigned to **4a** ($\delta = 361.6$ ppm) is accompanied by AX patterns: $\delta = 358.4$ and 55.1 ppm, $J = 9$ Hz (species **I**); $\delta = 135.2$ and 7.5 ppm, $J = 76$ Hz (species **II**); $\delta = 351.9$ and 38.5 ppm, $J = 107$ Hz (species **III**).

[(iPrMe$_2$Si)$_2$C=P]$_2$NtBu (**4b**): LDA (0.98 mL of a 2 M THF/heptane/ethylbenzene solution, 1 equiv) was added to a solution of **2b** (0.63 g, 1.96 mmol) in THF (7 mL) at −40 °C under a nitrogen atmosphere. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. ^{31}P NMR spectroscopic analysis of the solution showed quantitative formation of **3b** (^{31}P NMR (81 MHz, C_6D_6): $\delta = 404.3$ ppm). The formed *i*Pr$_2$NH and the solvent were removed in vacuo and the residue was dissolved in THF (10 mL). The solution of **3b** in THF was added slowly to a solution of **1b** (0.55 g, 1.96 mmol) in THF (10 mL) at −40 °C. The reaction mixture was allowed to warm slowly to room temperature. After 30 min, ^{31}P NMR spectroscopic analysis (81 MHz, C_6D_6) showed the formation of the desired product **4b** ($\delta = 365.8$ ppm). After removal of the lithium salt by filtration and the solvent in vacuo, ^{31}P NMR spectroscopic analysis showed, apart from **4b**, very small signals appearing as AX patterns (^{31}P NMR (81 MHz, C_6D_6): $\delta = 323.3$ and 50.1 ppm, J(P,P) = 167 Hz (0.5); $\delta = 136.4$ and 9.1 ppm, J(P,P) = 77 Hz (0.4)). Over a period of 12 h, the sample was kept at room temperature and afterwards the ^{31}P NMR spectrum showed that **4b** ($\delta_P = 365.8$ ppm) is accompanied by some rearranged species that show AX patterns: $\delta_P = 323.3$ and 50.1 ppm, J(P,P) = 167 Hz (7.3); $\delta_P = 354.7$ and 38.6 ppm, J(P,P) = 111 Hz (2.5), which relates with species **III**; $\delta_P = 136.4$ and 9.1 ppm, J(P,P) = 77 Hz (2.3), which relates with species **II**. After 9 d, **4b** and the compound related to species **II** are completely consumed.

*Reaction of **3b** with **1a***: LDA (0.8 mL of a 2 M THF/heptane/ethylbenzene solution, 1 equiv) was added to a solution of $(iPrMe_2Si)_2CPN(H)tBu$ (0.5 g, 1.6 mmol) in THF (8 mL) at −40 °C under a nitrogen atmosphere. The reaction mixture was then warmed to room temperature and was stirred for 1 h. ^{31}P NMR spectroscopic analysis of the solution showed quantitative formation of **3b** (^{31}P NMR (81 MHz, C_6D_6): $\delta = 404.3$ ppm). The formed *i*Pr$_2$NH and the solvent were removed in vacuo and the residue was dissolved in THF (10 mL). The solution of **3b** in THF was added slowly to a solution of **1a** (0.36 g, 1.6 mmol) in THF (5 mL) at −40 °C. The reaction mixture was allowed to warm slowly to room temperature. After 20 min, ^{31}P NMR spectroscopic analysis showed the formation of the desired mixed bisphosphaalkene (^{31}P NMR (81 MHz, C_6D_6): $\delta = 365.3$ and 361.7 ppm, ^{2}J(P,P) = 18 Hz). The lithium salt was removed by filtration and the solution was concentrated in vacuo followed by ^{31}P NMR spectroscopic analysis: the signals of the mixed bisphosphaalkene were accompanied by further AX patterns, among them one (^{31}P NMR (81 MHz, C_6D_6): $\delta = 136.32$ and 7.25 ppm, $J = 78$ Hz) closely related to species **II** in Scheme 3 (see also Scheme 4). After 2 d at room temperature, the species that represents the main product appeared in the ^{31}P NMR spectroscopy data at $\delta = 325.4$ and 49.4 ppm, $J = 163$ Hz.

*Compound **5***: Compound **1a** (0.9 g, 4 mmol) was added to a solution of **3a** [formed from **2a** (0.5 g, 2 mmol) and LDA (1 mL of a 2 M THF/heptane/ethylbenzene solution, 1 equiv) in tetraglyme (20 mL)] in tetraglyme (20 mL) at −40 °C under a nitrogen atmosphere. The reaction mixture was stirred for 2 h followed by NMR spectroscopic analysis. Removal of the solvent in vacuo furnished a red oil; in one experiment, red crystals (0.28 g, 25 %) suitable for an X-ray structure determination were obtained from the solution. ^{31}P NMR (81.02 MHz, C_6D_6, 25 °C): $\delta = 331.2$ ("t", line separation 28.8 Hz), −24.0 (dd, ^{1}J(P,P) = 175.7 Hz, ^{2}J(P,P) = 31.6 Hz), −17.2 ppm (dd, ^{1}J(P,P) = 175.7 Hz, ^{2}J(P,P) = 25.7 Hz); ^{13}C NMR (75 MHz), C_6D_6): $\delta = 150.1$ (ddd, ^{1}J(P,C) = 71.9 Hz, ^{2}J(P,C) = 15.5 Hz, ^{3}J(P,C) = 2.0 Hz), 60.5 (dd, ^{2}J(P,C) = 16.8, 13.2 Hz), 33.65 ("t", line separation = 10.2 Hz), 16.65 (ddd, ^{1}J(P,C) = 59.7 Hz, ^{2}J(P,C) = 19.6 Hz, ^{3}J(P,C) = 2.9 Hz), 12.5 (dd, ^{1}J(P,C) = 22.6 Hz, ^{2}J(P,C) = 6.2 Hz), 5.8 (d, ^{3}J(P,C) = 5.1 Hz), 5.6 (br s), 4.9 (dd, ^{3}J(P,C) = 5.5 Hz, ^{4}J(P,C) = 2.1 Hz), 4.2 (dd, ^{3}J(P,C) = 10.7 Hz, ^{4}J(P,C) = 1.3 Hz), 4.0 ppm (dd, ^{3}J(P,C) = 14.2 Hz, ^{3}J(P,C) = 4.0 Hz); elemental analysis calcd (%) for $C_{22}H_{54}NP_3Si_5$ (566.02): C 46.48, H 9.62, N 2.47; found: C ≤ 45.5, H ≤ 9.4, N 2.46–2.60.

[(iPrMe$_2$Si)$_2$C=P]$_2$N(1-Ada) (**8**): LDA (1.24 mL of a 2 M THF/heptane/ethylbenzene solution, 1 equiv) was added to a solution of **6** (0.98 g, 2.48 mmol) in THF (5 mL) at −40 °C. The reaction mixture was warmed to room temperature with magnetic stirring over 1 h. ^{31}P NMR spectroscopic analysis of the solution showed quantitative formation of **7** (^{31}P NMR (81 MHz, C_6D_6): $\delta = 405.8$ ppm). The resulting *i*Pr$_2$NH and the solvent were removed in vacuo and the residue was dissolved in THF (5 mL). The solution of **7** in THF was added slowly to a solution of **1b** (0.7 g, 2.48 mmol) in THF (5 mL) at −40 °C. After 15 min, the ^{31}P NMR spectra showed the formation of the desired bisphosphaalkene **8** (^{31}P NMR (81 MHz, C_6D_6): $\delta = 365.5$ ppm).The solution was kept for 24 h at −20 °C and yellow crystals were isolated (0.50 g, 32 %).^{1}H NMR (400 MHz, [D$_8$]toluene, −14 °C): $\delta = 2.09$–2.07 (pseudo-q, outer line dis-

tance = 8.9 Hz, 3H; C*H*-Ada), 1.89–1.87 (m, 1H; C*H*(CH$_3$)$_2$), 1.48–1.39 (m, 12H; C*H*$_2$-Ada), 1.28–1.05 (m, 13H; C*H*(C*H*$_3$)$_2$), 0.39–0.27 ppm (m, 12H; C*H*$_3$); ^{13}C NMR (100.6 MHz, [D$_8$]toluene, −14 °C): $\delta = 167.73$ (4 lines, X-part of AA′X-system $N = 98.7$, *C*=P), 62.73 (pseudo-t, $N = 10.4$ Hz; *C*-Ada), 45.90 (pseudo-t, $N = 18.8$ Hz; *C*H$_2$-Ada), 36.13 (s; *C*H$_2$-Ada), 30.80 (s; *C*H-Ada), 18.15 (br s) and 15.61 (s; CH(*C*H$_3$)$_2$), 14.78 (br s, *C*H(CH$_3$)$_2$), 12.59 (pseudo-t, outer line distance = 14.2 Hz; *C*H-(CH$_3$)$_2$), −1.54 and −1.82 ppm (br s; *C*H$_3$); ^{31}P NMR (162 MHz, [D$_8$]toluene, −14 °C): $\delta = 364.7$ ppm; MS (EI): *m*/*z* (%): 639 (10) [*M*]$^+$, 538 (80) [*M*−*i*PrMe$_2$Si]$^+$, 504 (100) [*M*−Ada]$^+$; elemental analysis calcd (%) for $C_{32}H_{67}NP_2Si_4$ (640.17): C 60.04, H 10.55, N 2.19; found: C 58.86, H 10.29, N 2.27.

Compound **8** is unstable at room temperature. The reaction was repeated and after filtration of the lithium salt and removal of the solvent the ^{31}P NMR spectrum showed, apart from **8**, some decomposition species: a compound analogous to species **II** (^{31}P NMR (81 MHz, C$_6$D$_6$): $\delta = 134.7$ and 7.6 ppm, *J*(P,P) = 81 Hz) and a compound characterized by the NMR spectroscopic pattern: ^{31}P NMR (81 MHz, C$_6$D$_6$) $\delta = 320.6$ and 46.7 ppm, *J*(P,P) = 173 Hz in small quantities. After one week at room temperature, **8** was completely consumed and the remaining species were as follows: ^{31}P NMR (81 MHz, C$_6$D$_6$): $\delta = 320.6$ and 46.7 ppm, *J*(P,P) = 173 Hz (main product), $\delta = 354.3$ and 35.3 ppm, *J*(P,P) = 112 Hz (analogue to species **III**), $\delta = 331.3$ and 34.2 ppm, *J*(P,P) = 127 Hz, the last two species with small intensities.

[(Me$_3$Si)$_2$C=P]$_2$N(Mes)* (***11 a***): LDA (0.94 mL of a 2 M THF/heptane/ethylbenzene solution, 1 equiv) was added to a solution of **9 a** (0.84 g, 1.87 mmol) in THF (10 mL) at −40 °C under a nitrogen atmosphere. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. ^{31}P NMR spectroscopic analysis of the solution showed quantitative formation of **10 a** (^{31}P NMR (81 MHz, C$_6$D$_6$): $\delta = 355.9$ ppm). The formed *i*Pr$_2$NH and the solvent were removed in vacuo and the residue was dissolved in THF (10 mL). The solution of **10 a** in THF was added slowly to a solution of **1 a** (0.42 g, 1.87 mmol) in THF (5 mL) at −40 °C, after which the reaction mixture was stirred for 20 min at room temperature. After removal of the lithium salt by filtration and the solvent in vacuo, ^{31}P NMR spectroscopic analysis of the oily residue showed the formation of the *sym*-**11 a** species (^{31}P NMR (81.02 MHz, C$_6$D$_6$, 25 °C): $\delta = 352.8$ ppm) and species *asym*-**11 a** (^{31}P NMR (81.02 MHz, C$_6$D$_6$, 25 °C): $\delta = 329.2$ and 323.1 ppm ^2J(P,P) = 7.4 Hz) and small quantities of **9 a** and [(Me$_3$Si)$_2$C=P]$_2$O. Isolation of pure **11 a** was not achieved except in one single experiment. After one week at room temperature, a decrease of the amount of *sym*-**11 a** in the mixture can be observed, whereas the amount of *asym*-**11 a** increases.

[(iPrMe$_2$Si)$_2$C=P]$_2$N(Mes)* (***11 b***): LDA (0.6 mL of a 2 M THF/heptane/ethylbenzene solution, 1 equiv) was added with a syringe to a solution of **9 b** (0.60 g, 1.19 mmol) in THF (10 mL) at −40 °C. The reaction mixture was warmed to room temperature with magnetic stirring over 1 h. ^{31}P NMR spectroscopic analysis of the solution showed quantitative formation of **10 b** (^{31}P NMR (81 MHz, C$_6$D$_6$): $\delta = 364.3$ ppm). The resulting *i*Pr$_2$NH and the solvent were removed in vacuo and the residue was dissolved in THF (10 mL). The solution of **10 b** in THF was added dropwise to a solution of **1 b** (0.33 g, 1.19 mmol) in THF (5 mL) at −40 °C. The solution was allowed to warm slowly to room temperature and after 50 min the ^{31}P NMR spectra showed the formation of *sym*-**11 b** (^{31}P NMR (81 MHz, C$_6$D$_6$): $\delta = 352.4$ ppm) and *asym*-**11 b** (^{31}P NMR (81 MHz, C$_6$D$_6$): $\delta = 331.7$ and 326.5 ppm, ^2J(P,P) = 13.5 Hz), with a ratio of about 5:2. After removal of the lithium salt and the solvent, an oily residue was obtained. Isolation of pure **11 a** was not achieved; a small ^{31}P NMR spectroscopic peak at $\delta = 354$ ppm, that is, slightly downfield from *sym*-**11 b**, is assigned to the oxide [(*i*PrMe$_2$Si)$_2$C=P]$_2$O. Within 2 d, a slight increase of the amount of *asym*-**11 b** is observed; the ratio of the two species *sym*/*asym* in solution is 5:3 and does not change for an extended period.

X-ray crystal-structure determinations: Data were registered using monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at low temperature. Diffractometer used: for **5**: Bruker SMART 1000 CCD; for **8**: Oxford Diffraction Xcalibur S. Absorption corrections were based on multi-scans. Structures were refined anisotropically on F^2 using the program SHELXL-97.[20] Hydrogen atoms were included using rigid idealised methyl groups (C−H = 0.98 Å, H-C-H = 109.5°) allowed to rotate but not tip, or a riding model for other H (C−H = 0.99 Å; sp^3 CH$_2$ and C−H = 1.0 Å; sp^3 CH). Structure **8** contains three formula units **8**·THF per asymmetric unit. CCDC-754788 (**5**) and 754789 (**8**) contain 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.

Compound 5: $C_{22}H_{54}NP_3Si_5$; $M_r = 566.02$; monoclinic; space group: $P2_1/n$; $a = 11.1309(10)$, $b = 16.9649(15)$, $c = 18.4626(16)$ Å; $\beta = 104.454(2)°$; $V = 3376.0(5)$ Å^3; $Z = 4$; $\rho_{\mathrm{calcd}} = 1.114$ mg m^{-3}; $T = 133(2)$ K; orange prism. Of 39 724 reflections measured, 10 280 were independent ($R_{\mathrm{int}} = 0.1464$). The final $wR2$ was 0.1613 (all data).

Compound 8: $C_{36}H_{75}NOP_2Si_4$; $M_r = 712.27$; monoclinic; space group: $P2_1/c$; $a = 10.7496(2)$, $b = 34.0778(8)$, $c = 35.1768(8)$ Å; $\beta = 95.5588(18)°$; $V = 12825.5(5)$ Å^3; $Z = 12$; $\rho_{\mathrm{calcd}} = 1.107$ mg m^{-3}; $T = 100(2)$ K; yellow tablet. Of 334 611 reflections measured, 26 186 were independent ($R_{\mathrm{int}} = 0.0749$). The final $wR2$ was 0.1640 (all data).

Computations: The computations were carried out with the Gaussian 03 program package.[21] All structures were optimised with two different basis sets (3-21G(*) for pre-optimisation and 6-31+G*) using the B3LYP functional. Vibrational analysis was performed on each of the optimised structures to check whether the stationary point located is a minimum of the potential energy hypersurface or a first-order saddle point (in the case of transition states). For the optimised structures, the stability of the wavefunction was tested; no instability was found. At the saddle points located, IRC calculations were performed to locate the minima connected by the transition structure. To investigate the convergence of the basis set, calculations have been performed on the optimised geometries single point with the larger 6-311+G** basis set using the B3LYP functional, and the difference was found to be negligible. Further single-point calculations have been carried out at the MPW1K/6-311+G** and MP2/6-311+G** or MP2/6-31+G* levels depending on the size of the molecules. NMR spectroscopic chemical shifts were computed with the gauge-independent atomic orbital (GIAO) method at the B3LYP/cc-pVTZ and B3LYP/IGLO-III[22] levels (see the Supporting Information). The ^{31}P shifts were determined following the method in ref. [23]. For visualisation of the molecules, the Molden program was used.[24]

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