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ARTICLE

Sterically Tuned *P*-Phosphanylamino Phosphaalkenes $(Me_3Si)_2C{=}PN(R)PPh_2$ and $(iPrMe_2Si)_2C{=}PN(R)PPh_2$

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Abstract. Deprotonation of the aminophosphanes $Ph_2PN(H)R$ **1a**–**1h** [*R* = *t*Bu (**1a**), 1-adamantyl (**1b**), *i*Pr (**1c**), CPh_3 (**1d**), Ph (**1e**), 2,4,6-$Me_3C_6H_2$ (Mes) (**1f**), 2,4,6-$tBu_3C_6H_2$ (Mes*) (**1g**), 2,6-$iPr_2C_6H_3$ (DIPP) (**1h**)], followed by reactions of the phosphanylamide salts $Li[Ph_2PNR]$ **2a**, **2b**, **2g**, and **2h** with the *P*-chlorophosphaalkene $(Me_3Si)_2C{=}PCl$, and of **2a**–**2g** with $(iPrMe_2Si)_2C{=}PCl$, gave the isolable *P*-phosphanylamino phosphaalkenes $(Me_3Si)_2C{=}PN(R)PPh_2$ **3a**, **3b**, **3g**, and $(iPrMe_2Si)_2C{=}PN(R)PPh_2$ **4a**–**4g**. ^{31}P NMR spectra, supported by X-ray structure determinations, reveal that in compounds **2a**, **2b**, **3a**, and **3b**, with bulky N-alkyl groups the $Si_2C{=}P{-}N{-}P$ skeleton is non-planar (orthogonal conformation), whereas **3g**, **3h**, and **4g** with bulky N-aryl groups exhibit planar conformations of the $Si_2C{=}P{-}N{-}P$ skeleton. Solid **3g** and **4g** exhibit *cisoid* orientation of the planar C=P–N–C units (planar I) but in solid **3h** the *transoid* rotamer is present (planar II). From **3g**, **4d**, and **4g** mixtures of rotamers were detected in solution by pairs of ^{31}P NMR patterns (**3h**: line broadening).

Introduction

We have recently studied the "hybrid" *P*-phosphanylamino phosphaalkene ligands $(Me_3Si)_2C{=}PN(R)PR'_2$ (Scheme 1, **A**) with the intention of combining the features of classic small bite angle iminobisphosphane "PNP" ligands $RN(PR'_2)_2$ (**B**)[1] with those of thermally more labile amino-bridged bis-phosphaalkenes (**C**).[2]

The enhanced electrophilicity of the phosphaalkene phosphorus atom of the coordinated type **A** chelate ligand $(Me_3Si)_2C{=}PN(1\text{-}Ada)PPh_2$ led to exceptional Cl→P coordination (chlorotropy); reactions with $PtCl_2$ and $PdCl_2$ led to uncharged complexes $M[(Me_3Si)_2C{=}P(Cl)N(1\text{-}Ada)PPh_2]_2$ (*M* = Pd, Pt) that involved anionic chelate ligands $[(Me_3Si)_2C{=}P(Cl)N(1\text{-}Ada)PPh_2]^-$ with P–Cl bonds.[3] Subsequently, reactions of type **A** ligands with Rh^I chlorido complexes were shown to involve RhCO-assisted P–C coupling reactions with loss of $(Me_3Si)_2C{=}C{=}O$, leading from the type **A** compounds to dianionic tetradentate ligand units in the coordination sphere of an $Rh^{III}Cl$ unit.[4]

To obtain synthetic access to type **A** ligands, we initially attempted to use metallated *P*-aminophosphaalkenes (1-aza-2-phosphaallyl anions)[5,6,7] for P–N coupling reactions with chlorodiphenylphosphane, analogous to P–N coupling reactions of metallated *P*-aminophosphaalkenes with *P*-chlorophosphaalkenes,[2,8] which are known to deliver the "doubly unsaturated" type **C** ligands (Scheme 2, top).

Towards chlorodiphenylphosphane, however, the 1-aza-2-phosphaallyl anions of $Li[(Me_3Si)_2C{=}PNR]$ (*R* = *t*Bu,[2,6,7] Mes* [6]) acted as *P*-nucleophiles leading, according to ^{31}P NMR spectroscopic data, preferentially to the type **D** *P*-diphenylphosphanylphosphorane isomers $[(Me_3Si)_2C{=}](RN{=})P{-}PPh_2$.[3,6–8] From $Li[(Me_3Si)_2C{=}PNtBu]$ with chlorodiisopropylphosphane, the corresponding type **D** product was obtained, accompanied by the isomeric *P*-phosphanylazaphosphirane structure (type **E**) according to ^{31}P NMR spectroscopy. With chloro(isopropyl)*t*-butylphosphane as substrate for $Li[(Me_3Si)_2C{=}PNtBu]$, the reaction was selective leading to the single crystalline product $(Me_3Si)_2C{=}PN(tBu)P(tBu)(iPr)$, which was characterized by X-ray crystallography as a new example of the type **D** structure (Scheme 2, center).[7] Only one compound of the phosphanylphosphorane type **D** structure had previously been investigated crystallographically; it was synthesized by $(Me_3Si)_2C$ transfer from a carbenoid precursor to the bulky *P*-phosphanyliminophosphane $tBu_2PP{=}NMes^*$ (Scheme 2, bottom).[9] Since $Li[(Me_3Si)_2C{=}PNtBu]$ acts selectively as a *P*-nucleophlile towards diphenyl and dialkyl chlorophosphanes, we chose, as an alternative access to type **A** PNP ligands, the *inverse* route using metallated aminophosphanes and *P*-chlorophosphaalkenes (Scheme 3).[3] Fortunately, metallated aminophosphanes such as $Li[Ph_2PN(1\text{-}Ada)]$[3] act towards the *P*-chlorophosphaalkene $(Me_3Si)_2C{=}PCl$ selectively as *N*-nucleophiles, delivering the desired type **A** ligands. In the following we presemt some novel synthetic results concerning this reaction route. These syntheses provide mono-unsaturated bidentate diphenylphosphanylamino-phosphaalkene ligands (type **A**) of varied steric encumbrance.[8]

Results and Discussion

Aminophosphanes

Various aminophosphanes $Ph_2PN(H)R$[10] **1a**–**1h** [*R* = *t*Bu (**1a**), 1-adamantyl (**1b**), *i*Pr (**1c**), CPh_3 (**1d**), Ph (**1e**), 2,4,6-

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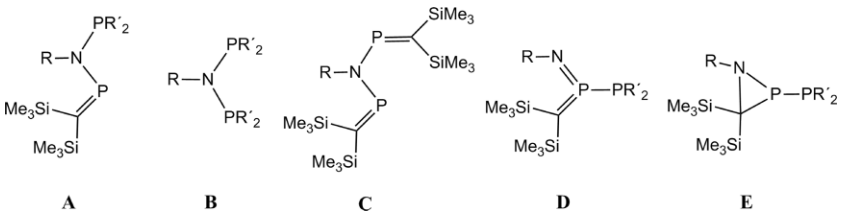
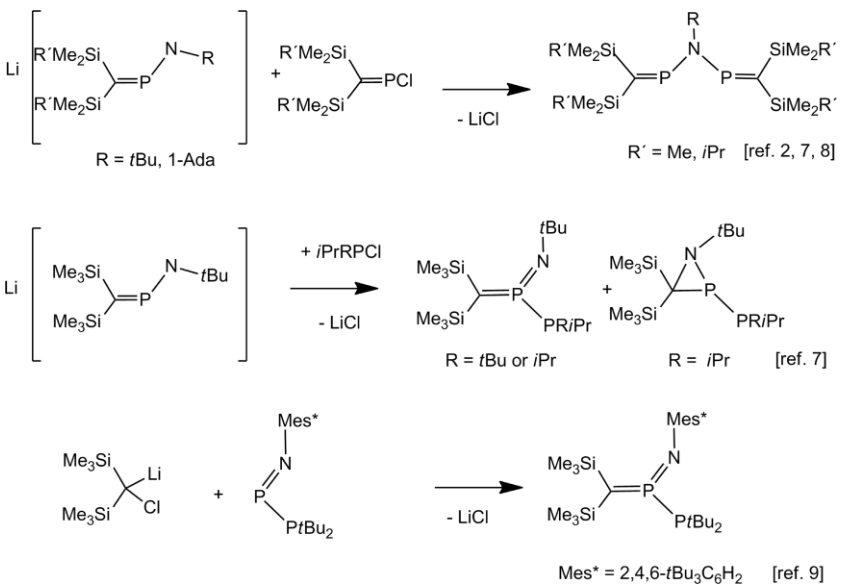
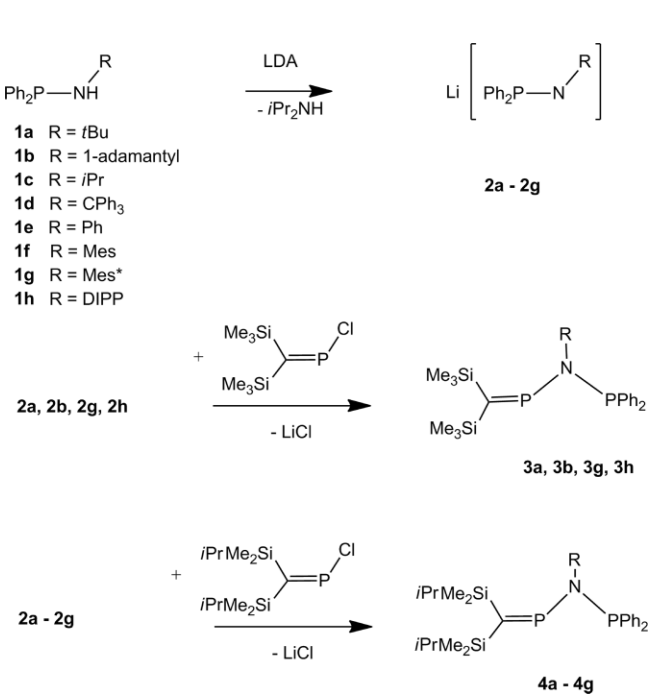


Scheme 1. Various types of iminoorganophosphorus species with P–N–P or P–P–N backbones.



Scheme 2. Access to PNP and PPN species via (top and center)[2,7] N–P and P–P coupling reactions of 1-aza-2-phosphaallyl anions; (below) the reaction leading to the first low-coordinated phosphanyl(alkylidene)(imino)phosphorane.[9]



Scheme 3. The route to *P*-phosphanylamino phosphaalkenes **3** and **4**.

$Me_3C_6H_2$ (Mes) (**1f**), 2,4,6-$tBu_3C_6H_2$ (Mes*) (**1g**), 2,6-$iPr_2C_6H_3$ (DIPP) (**1h**)], including a few examples with particularly bulky substituents, were chosen as starting materials for metallation reactions. The solid-state structures of **1b**, **1f**, and of oxidized **1f**(P=O) were determined by X-ray crystallography (see Scheme 3, Experimental Section, Table 3, and Figures S1–S3, Supporting Information).

Synthesis of Phosphanylamino Phosphalkenes

Aminophosphanes were deprotonated at –40 °C with lithiumdiisopropyl amide (LDA) in mixtures of solvents containing THF; only for **1d** *n*BuLi was used. Solutions of the lithium derivatives **2a**–**2h** were added dropwise to the *P*-chlorophosphaalkenes $(Me_3Si)_2C{=}PCl$ and / or $(iPrMe_2Si)_2C{=}PCl$ at –40 °C leading with (partial) precipitation of LiCl to the *P*-diphenylphosphanylamino phosphaalkenes **3** or **4** (Scheme 3), which are soluble in hydrocarbons.

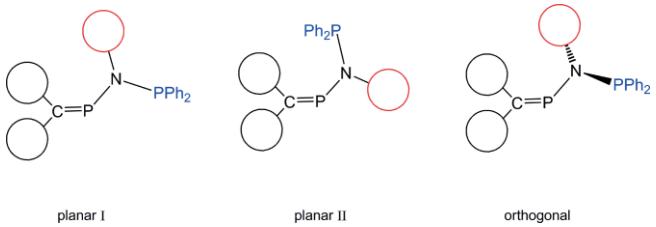
All products were identified by ^{31}P NMR, but only **3a**, **3b**, **3g**, **4b**, and **4e** were isolated in bulk as yellow solids. From all four products **3** (**3a**, **3b**, **3g**, and **3h**) single crystals were obtained, even though the bulk of **3h** was an impure solid. Similarly a single crystal of **4g** was picked from an impure solid sample. *P*-Diphenylphosphanylamino phosphaalkenes **3** and **4**

are air- and moisture-sensitive compounds; pure samples can be stored under inert gas for an extended time.

NMR Spectroscopic Characterization

^{31}P NMR spectroscopic data of compounds **3** and **4** are collected in Table 1. ^{31}P- and ^{13}C-spectroscopic investigations on related *P*-aminophosphaalkenes $(Me_3Si)_2C{=}PN(R)R'$ (*R* = alkyl, *R'* = H, alkyl, or trimethylsilyl) have revealed that favorable $n(N)\rightarrow\pi(P{=}C)$ conjugation in 3-center, 4-electron π-bond systems correlates with significant upfield shifts in relation to isolated P=C bonds.[5] *P*-Amino groups with two very bulky subsituents such as *tert*-butyl, trimethylsilyl, or 2,2,6,6-tetramethylpiperidyl, however, tend for steric reasons to conformations exhibiting orthogonal orientation of the amino groups with respect to the phosphaalkene plane $Si_2C{=}P$.[5,11] When one of the bulky substituents is an aryl group, such as 2,4,6-$tBu_3C_6H_2$– (Mes*), the aromatic ring plane of the latter can rotate into a position orthogonal to the nitrogen plane, allowing the latter to adopt a conformation with nearly coplanar phosphaalkene and nitrogen planes; in the related compound $(Me_3Si)_2C{=}PN(Mes^*)SiMe_3$ the dihedral angle between the amino group and the nodal plane $Si_2C{=}P$ of the double bond is 11.2°.[11]

In our choice of *P*-diphenylphosphanylamino phosphaalkenes, the 1-adamantyl, *tert*-butyl and trityl groups are very bulky alkyls, and the PPh_2 groups are sterically comparable to $SiMe_3$ or $SiMe_2Ph$. All aminophosphaalkenes $(Me_3Si)_2C{=}PN(H)R$ and $(iPrMe_2Si)_2C{=}PN(H)R$ that are related to **3a**, **3b**, or **4a**–**4g** exhibit ^{31}P-NMR shifts between δ = 310 and 326 ppm and ^{13}C NMR shifts between 70 and 77 ppm,[8] whereas among the phosphanylamino phosphaalkenes **3** and **4**, the ^{31}P(=C) nuclei of the 1-adamantyl and *tert*-butyl derivatives **4a**, **4b** exhibit significantly deshielded resonances in ^{31}P and ^{13}C NMR, indicating a loss of $n(N)\rightarrow\pi(P{=}C)$ conjugation (Scheme 4 and Experimental Section).[5,11] The exchange of *R* = *t*Bu in **4a** for *R* = *i*Pr in **4c** leads in the ^{31}P NMR to a 40 ppm upfield shift of the ^{31}P(=C) nucleus, whereas the $^{31}P(Ph_2)$ nucleus is scarcely affected (Table 1).



Scheme 4. Idealised coplanar and orthogonal conformations of phosphanylamino phosphaalkenes, Si (black circles) = Me_3Si or $iPrMe_2Si$, *R* (red Circles) = alkyl or aryl. Left: planar I, center: planar II, right: orthogonal.

In the cases of the bulky aromatic substituents and of the trityl group, two species are present in solution, as indicated by two sets of AM patterns in the ^{31}P NMR spectra of **3g**, **4g** (*R* = Mes*) and of **4d** (*R* = CPh_3), and by line broadening in the spectra of **3h** and **4f**. The resonances of the ^{31}P(=C) nuclei from the two AM patterns of each of the compounds **3g** and **4g** differ by only 7 ppm, whereas the resonances of the $^{31}P(Ph_2)$ nuclei differ by about 20 ppm. The varying magnitudes of the NMR couplings ^2J(P,P) in the range from 6.6 (**4a**) to 67.5 Hz (**4e**) allow to suggest different relative orientations of the phosphorus lone pairs in the P–N–P moieties.[10a] The difference between the coupling constants ^2J(P,P) of the two species of **3g** is 14 Hz, but only 4 Hz in the case of **4g**. These differences reflect not only the different conformations of the C=P–N–P moieties (planar I or II, see Scheme 4), but also possible differences in the rotational preferences of the N–PPh_2 groups (rotation around this P–N bond, see Supporting Information, Figure S1).[10a]

Oxidation of the PPh_2 phosphorus atom of **3b** [δ^{31}P = 373.5 and 37.7 ppm, ^2J(P,P) = 12.0 Hz, δ^{13}C(=P) 190.5, ^1J(P=C) = 98.8 Hz] with selenium leads to the compound $(Me_3Si)_2C{=}PN(1\text{-Ada})P(=Se)Ph_2$ [**3b**(P=Se), δ^{31}P = 350.4 and 45.7 ppm,

Table 1. ^{31}P NMR spectroscopic data of *P*-phosphanylamino phosphaalkenes.

	δ = ^{31}P(=C) /ppm	δ = $^{31}PPh_2$ /ppm	$\lvert^2J(P,P)\rvert$ /Hz
$(Me_3Si)_2C{=}PN(R)PPh_2$			
3a (*R* = *t*Bu)	372.9	44.4	11.5
3b (*R* = 1-adamantyl)[3]	374.0	37.7	12.1
3b(P=Se) (*R* = 1-adamantyl)	350.4	45.7 (P=Se)	
3g (*R* = Mes*)	330.5	74.0	7.1
	337.7	55.1	21.0
3h (*R* = DIPP)	335.8 (broad), 58.8 (broad)	not resolved	
3j (*R* = CH_2Ph)[4,12]	349.3	59.4	39.4
$(iPrMe_2Si)_2C{=}PN(R)PPh_2$			
4a (*R* = *t*Bu)	382.3	47.0	6.6
4b (*R* = 1-adamantyl)	385.7	38.3	10.0
4c (*R* = *i*Pr)	342.7	43.6 (broad)	13.8
4d (*R* = CPh_3)	366.5	25.6	32.8
	361.5	15.4	40.0
4e (*R* = Ph)	351.3	60.9	67.5
4f (*R* = Mes)	331.4 (broad)	63.8 (broad)	not resolved
4g (*R* = Mes*)	341.2	72.6	30.5
	337.7	50.2	26.2

$\delta^{13}C(=P)$ = 183.4 ppm, $^{1}J(P,C)$ = 101.8 Hz], which does not exhibit a resolvable coupling $^{2}J(P,P)$.

Structure Determinations

The molecular structures of compounds **3a**, **3b**, **3g**, **3h**, **4b**, and **4g** are presented in Figure 1, Figure 2, Figure 3, Figure 4, Figure 5, and Figure 6. The structures can be assigned on the basis of the relative orientations of the P*N*CP and Si_2C=PN planes to the idealized cases of *planar I* or *II* or *orthogonal* (Scheme 4). According to structure determinations the topologies of the backbones of the compounds with NMes* groups (**3g**, **4g**) (the crystallized rotamers) are related to that of Chernegas' compound $(Me_3Si)_2C$=PN(Mes*)$SiMe_3$,[11] corresponding to the planar I conformation with *cisoid* orientation of the P=*C*- and Mes*-C*ipso* carbon atoms at the P–N bond [torsion angles C1P1NP2 179.44(7)° (**3g**) and 179.55° (**4g**)]. Compound **3h**, with an N-DIPP group, however, exhibits a slightly distorted planar II conformation with a *transoid* orientation of the P=C- and DIPP*-C*ipso* carbon atoms at the P–N bond [torsion angle C1P1NP2 16.25(11)°]. In this structure, the angle P1–N–C*ipso* is particularly narrow, compared with the other compounds [110.8° (**3h**) versus 116.5° (**3b**) to 128.38° (**4g**)], whereas the angles P1–N–P2 (125.8°) and P2–N–C*ipso* (123.4°) are unusually wide (for selected distances and angles, see Table 2).

The large angles P1–N–C*ipso* of solid **3g** and **4g** may reflect the repulsions between bulky aryl groups and the neighboring pair of trialkylsilyl groups.[11]

The structures of the compounds with N-*t*Bu and with N-1-Ada groups (**3a**, **3b**, and **4b**) exhibit distorted *orthogonal* conformations. The conformational differences *planar* vs. *orthogonal* are reflected in the interplay of the P–N distances of C=PN and $NPPh_2$ groups in phosphanylamino phosphaalkenes, whereas the P=C distances are very similar at about 1.66 Å. In

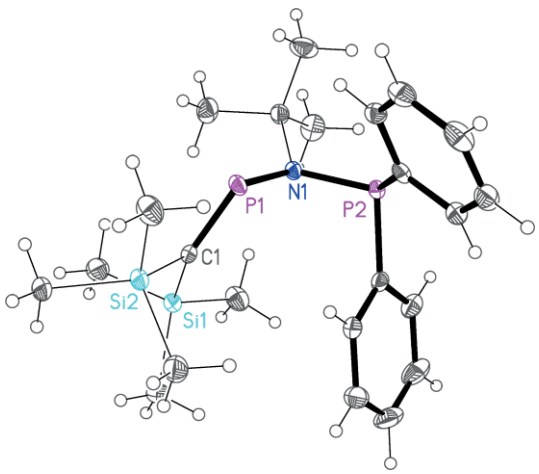


Figure 1. Structure of compound **3a** in the crystal. Ellipsoids represent 50% probability levels.

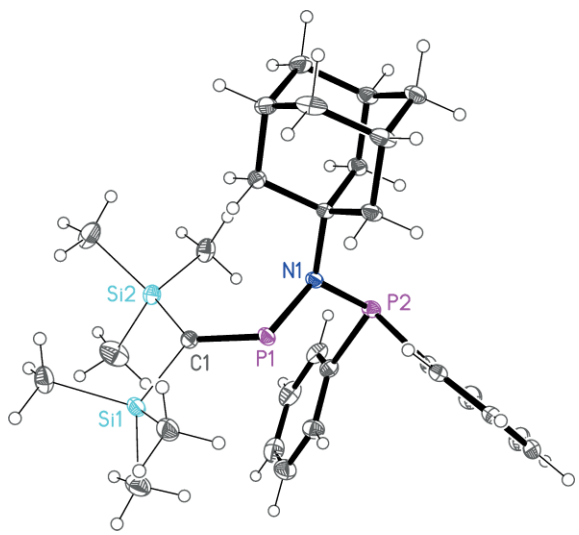


Figure 2. Structure of compound **3b** in the crystal. Ellipsoids represent 50% probability levels.

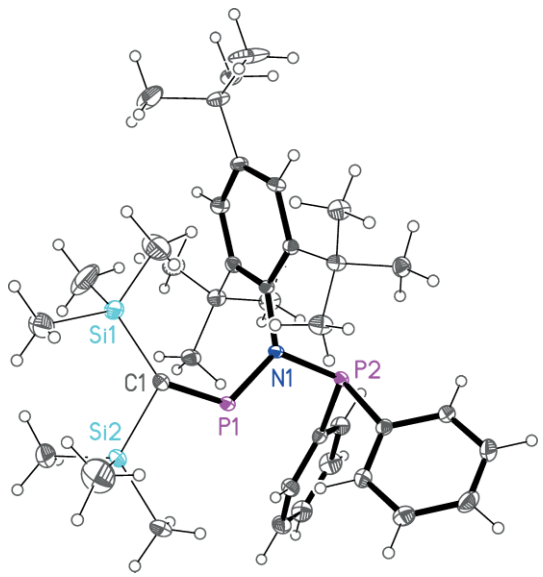


Figure 3. Structure of compound **3g** in the crystal. Ellipsoids represent 50% probability levels.

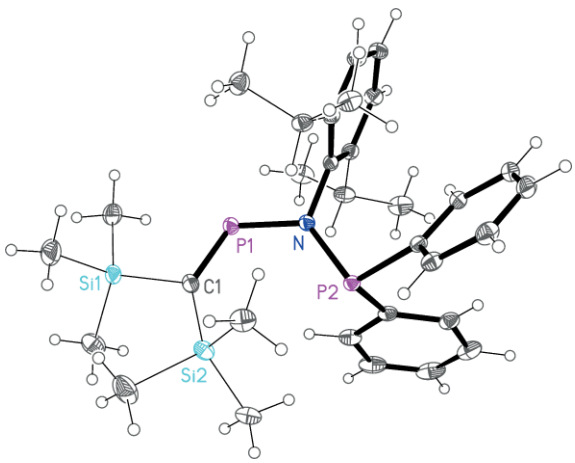


Figure 4. Structure of compound **3h** in the crystal. Ellipsoids represent 30% probability levels.

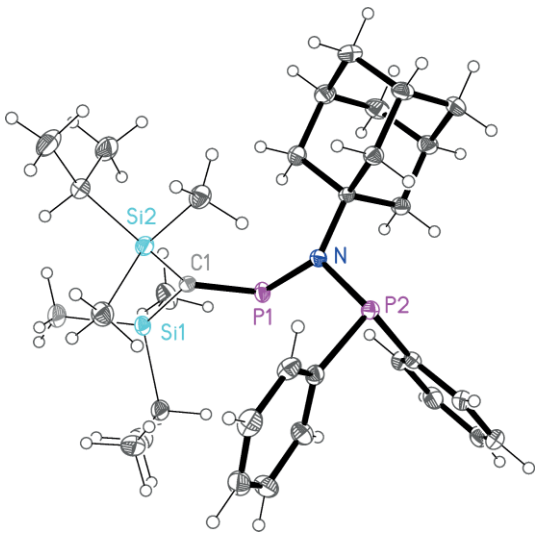


Figure 5. Structure of compound **4b** in the crystal. Ellipsoids represent 50% probability levels.

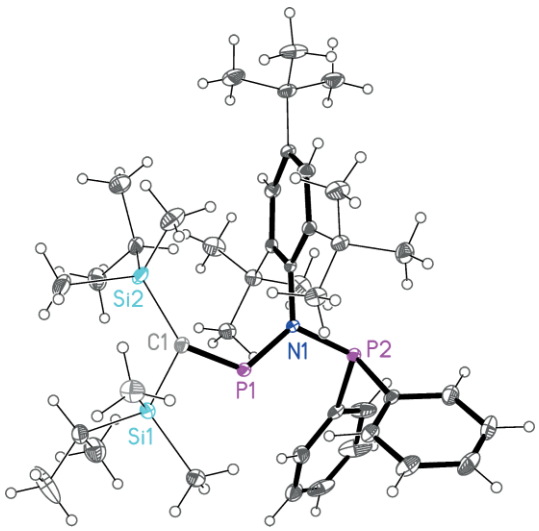
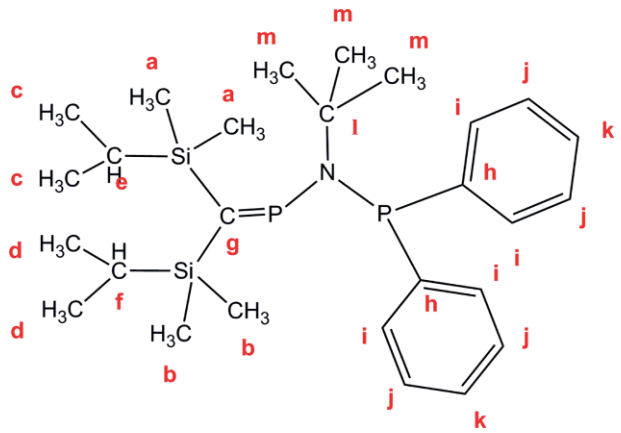


Figure 6. Structure of compound **4g** in the crystal. Ellipsoids represent 50% probability levels. Only one position of the disordered $SiMe_2iPr$ group is shown.

the structures **3a**, **3b**, and **4b** with large torsion angles C1–P1–N–P2 (105–111°) and slightly pyramidalized nitrogen atoms (angle sums of 352°), the distances between the nitrogen and the phosphaalkene phosphorus atoms (about 1.74 Å, single bond) are slightly longer than those of the P–N single bonds involving the PPh_2 groups (about 1.72 Å). However, in the



Scheme 5. Atom designation for the NMR assignment (bold letters) proposed for the ^{1}H and ^{13}C nuclei of **4a** and related compounds.

structures assigned to the planar I and II types, P–N distances of the C=PN moieties are shorter (1.70–1.71 Å) and the P–N bonds involving the PPh_2 groups are lengthened to 1.74 Å (**3h**), 1.76 Å (**4g**), and 1.77 Å (**3g**). These effects, together with the ^{31}P-NMR shifts of the latter (downfield from those of **3a**, **3b** and **4a**, **4b**) correlate with some degree of N–P=C conjugation. *N*-aryl conjugation does not play a role, since the aromatic planes of the bulky *N*-aryl groups in **3g**, **3h**, and **4g** are not coplanar with the planar C1–P1–N–P2 backbones of these phosphanylamino phosphaalkenes.

Conclusions

P-Phosphanylamino phosphaalkene ligands ($R'Me_2Si)_2C$=PN(*R*)PPh_2 [*R* = Me (**3**), *i*Pr (**4**)] are available from reactions of lithium diphenylphosphanylamides Li[Ph_2PNR] **2a–2h** [*R* = *t*Bu (**1a**), 1-adamantyl (**1b**), *i*Pr (**1c**), CPh_3 (**1d**), Ph (**1e**), 2,4,6-$Me_3C_6H_2$ (Mes) (**1f**), 2,4,6-$tBu_3C_6H_2$ (Mes*) (**1g**), 2,6-$iPr_2C_6H_3$ (DIPP) (**1h**)] with *P*-chlorophosphaalkenes ($R'Me_2Si)_2C$=PCl (*R′* = Me, *i*Pr). Crystal structure determinations of the monounsaturated bidentate PNP ligands **3a**, **3b**, **3g**, **3h**, **4b**, and **4g** allow classification of the structures, according to the relative orientations of the P*N*CP and Si_2C=PN planes, to the idealized cases of *planar* (coplanar phosphaalkene and nitrogen planes: **3g**, **3h**, **4g**) and *orthogonal* (phosphaalkene and nitrogen planes with large torsion angles: **3a**, **3b**, **4b**). **3g** and **4g** (*R* = Mes*) exhibit *cisoid* orientation of the P=*C*- and Mes*-*Cipso* carbon atoms at the P–N bond (*planar I*), whereas **3h** (*R* = DIPP) crystallized with *transoid* orientation of the P=*C*- and DIPP*-*Cipso* carbon atoms at the P–N

Table 2. Selected distances /Å and angles /° within the backbones C1–P1–N(–C)–P2 of compounds **3** and **4**.

	d(P=C)	*d*(P1–N)	*d*(P2–N)	<C1–P1–N	<P1–N–C	<P2–N–C	<P1–N–P2
3a	1.664(14)	1.748(12)	1.724(11)	112.8(7)	119.5(9)	115.4(9)	116.8(7)
3b	1.665(2)	1.748(12)	1.721(11)	111.5(5)	116.5(7)	118.37(7)	119.3(5)
3h	1.662(14)	1.706(11)	1.742(11)	116.9(6)	110.8(8)	123.4(8)	125.8(6)
3g	1.663(11)	1.712(9)	1.771(9)	120.9(5)	126.1(7)	116.6(7)	117.2(5)
4a	1.6609(12)	1.7393(10)	1.7227(10)	113.85(5)	118.89(5)	115.19(7)	117.67(6)
4g	1.6609(11)	1.7077(9)	1.7603(9)	121.55(5)	128.38(7)	113.24(7)	118.38(5)

bond (*planar II*). The structures of the compounds with N-*t*Bu and with N-1-Ada groups (**3a**, **3b**, and **4b**) exhibit distorted *orthogonal* conformations, comparable to aminophosphaalkenes with $N(SiMe_3)_2$ groups.[5] The conformational differences *planar* versus *orthogonal* are reflected in the interplay of the P–N distances of C=PN and $NPPh_2$ groups in phosphanylamino phosphalkenes whereas the P=C distances are close to invariant at 1.66 Å. The lack of favorable π-overlap between the nitrogen lone pairs and the P=C π orbitals in the *orthogonal* conformations of **3a**, **3b**, and **4b** with *N*-PPh_2 and bulky *N*-alkyl groups is also reflected in particularly low-field chemical shifts of the ^{31}P(=C) nuclei in the ^{31}P NMR spectra of these ligands.

Experimental Section

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

Aminophosphanes: All aminophosphanes Ph_2PNHR except the 1-adamantyl, the trityl, the mesityl, and the 2,6-diisopropylphenyl (DIPP) derivatives (**1b**, **1d**, **1f**, **1h**) were prepared according to published methods.[10]

Ph_2PN(H)1-Ada (1b): A solution of adamantylamine (1.73 g, 11.43 mmol) in 35 mL pentane was treated with triethylamine (2.4 mL, 17 mmol) and chlorodiphenylphosphane (1.1 g, 5 mmol) at room temperature. After 1 h, a white precipitate had separated from the solution. Evaporation of all volatiles at reduced pressure provided **1a** (5.34 g, 85 %) as a white solid, m.p. 75–76 °C. **^{1}H NMR** (200.1 MHz, C_6D_6): δ = 7.5–7.4 and 7.2–7.07 (multiplets, aryl H), 1,92 [d, J(P,H) = 3.7 Hz, Ada], 1.78 (s, br., Ada), 1.53 (s, br., Ada) ppm. **^{13}C NMR** (50.32 MHz, C_6D_6): δ = 144.3 [d, ^1J(P,C) = 13.3 Hz, *ipso*-C], 130.9 [d, ^3J(C,P) = 20.4 Hz, *m*-C], 128.0 [s, *p*-C], 127.9 [d, ^2J(C,P) = 6.2 Hz, *o*-C], 50.9 [d, ^2J(C,P) = 18.0 Hz, Ada], 45.8 [d, J(C,P) = 8.9 Hz, Ada], 36.2 (s, Ada), 29.9 [d, J(C,P) = 0.9, Ada] ppm. **^{31}P NMR** (81.02 MHz, C_6D_6): δ = 18.9 ppm. $C_{22}H_{26}NP$ (M = 335.42, exact mass = 335.18 g·mol^{-1}): calcd. C 78.78, H 7.81, N 4.18 %; found C 78.33, H 7.82, N 4.29 %. **MS** (EI, 90 eV) *m*/*z* (%): 335 (100) [M^+], 135 (26, M^+ - Ph_2PNH).

Ph_2PN(H)CMe_3 (1d): A solution of *C*-triphenylmethylamine (1.51 g, 5,81 mmol) in 10 mL THF was treated at –50 °C dropwise with *n*-butyllithium (2.5 M solution in hexane, 2.3 mL, 5.81 mmol). The stirred solution was allowed to warm up to room temperature and after 2 h the resulting solution was added at –40 °C dropwise to chlorodiphenylphosphane (1.28 g, 5.81 mol) in 10 mL THF. After warming up to room temperature the lithium salt residue was removed by filtration. Evaporation of the solvent at reduced pressure provided **1d** (2.07 g, 81 %) as a yellowish solid, m.p. 118–120 °C. **^{1}H NMR** (200.1 MHz, C_6D_6): δ = 7.5–7.03 (multiplets, aryl H), 3.07 (s, H–N) ppm. **^{13}C NMR** (50.32 MHz, C_6D_6): δ = 146.8 [d, J(C,P) = 3.5 Hz], 142.1 [d, J(C,P) = 12.7 Hz], 130.6 [d, J(C,P) = 20.8 Hz], 128.3 [d, J(C,P) = 2.3 Hz], 127.5 [d, J(C,P) = 8.9 Hz], 127.1 (s), 125.9 (s), 70.5 [d, J(C,P) = 18.8 Hz]. **^{31}P NMR** (81.02 MHz, C_6D_6): δ = 27.1 ppm. $C_{31}H_{26}NP$ (M = 443.52): calcd. C 83.95, H 5.91. N 3.16 %; found C 80.95, H 5.90, N 3.18 %.

Ph_2PN(H)(2,4,6-$Me_3C_6H_2$) (1f): Similarly to the preparation of **1b**, chlorodiphenylphosphane (3.52 g, 15.97 mmol) in 75 mL pentane with triethylamine (4.5 mL, 31.0 mmol) and 2.52 g (11.43 mmol) 2,4,6-trimethylaniline gave after 12 h at room temperature 3.1 g (61 %) yellowish **1f**, m.p. 87–89 °C. Single crystals suitable for X-ray diffraction were grown from pentane. **^{1}H NMR** (200.1 MHz, C_6D_6):): δ = 7.5–6.73 ppm (multiplets, aryl H), 3.61 [d, J(P,C) = 8.5 Hz, H–N], 2.2–2.1 (m, *o*-CH_3), 1.93 (s, *p*-CH_3). **^{13}C NMR** (50.32 MHz, C_6D_6): δ = 142.7 [d, J(P,C) = 15.7 Hz], 140.3 [d, J(P,C) = 14.2 Hz], 130.6 [d, J(C,P) = 3.6 Hz], 129.2 [d, J(P,C) = 17.4 Hz], 128.8 (s), 128.5(s), 128.2 [d, J(P,C) = 6.3 Hz], 20.2 [d, J(P,C) = 3.9 Hz], 18.8 [d, J(P,C) = 6.0 Hz], 17.1(s). **^{31}P NMR** (81.02 MHz, C_6D_6):): δ = 36.6. From an NMR tube a few single crystals of the oxide $Ph_2P(=O)N(H)$(2,4,6-$Me_3C_6H_2$) [**1f**(P=O)] were isolated.

Ph_2PN(H)(2,6-$iPr_2C_6H_3$) (1h): Chlorodiphenylphosphane (3 g, 13 mmol) in 60 mL pentane reacted with with 2,6-diisopropylaniline (4.6 g, 26 mmol) for 2 d at room temperature. The white precipitate was filtered off and the solvent evaporated at reduced pressure, to give 3.6 g (95 %) **1h** as a white solid. **^{1}H NMR** (200.1 MHz, C_6D_6): δ = 7.5–7.03 ppm (multiplets, aryl H), 3.82 [d, J(C,P) = 8.1 Hz], H-N), 3.0 (m, CH), 1.06 (s, CH_3), 1.04 (s, CH_3). **^{13}C NMR** (50.32 MHz, C_6D_6): δ = 142.5 (s), 142.4 [d, J(C,P) = 19.1 Hz], 139.7 [d, J(C,P) = 12.6 Hz], 131.3 [d, J(C,P) = 20.6 Hz], 128.8 (s), 128.3 [d, J(C,P) = 6.3 Hz], 122.7 (s), 118.4 (s), 27.0 [d, J(C,P) = 14.7 Hz], 23.8 (s, CH_3). **^{31}P NMR** (81.02 MHz, C_6D_6): δ = 43.1 ppm.

Reactions of Metallated Aminophosphanes with $(Me_3Si)_2C$=PCl and with $(i$PrMe$_2$Si$)_2C$=PCl; General Procedure: To the solution of an alkyl- or arylaminodiphenylphosphane **1** in 10 mL of THF at –40 °C was added dropwise an equimolar amount of LDA (2 M *solution* in THF-heptane-ethylbenzene); subsequently the reaction mixture was allowed to warm up to room temperature. A singlet signal in the ^{31}P NMR spectrum of the reaction mixture confirmed the presence of the deprotonated species **2**. After removal of the volatiles in vacuo the residue was dissolved in THF and added dropwise at –40 °C to a solution of $(Me_3Si)_2C$=PCl or of $(i$PrMe$_2$Si$)_2C$=PCl in THF. After warming up slowly to room temperature and further stirring for 1 h, all volatiles were removed in vacuo and the residue was taken up in pentane. Removal of LiCl by filtration through Celite® 535, followed by concentrating the pentane solution to dryness, furnished the products **3** [from $(Me_3Si)_2C$=PCl] or **4** [from $(i$PrMe$_2$Si$)_2C$=PCl].

***P-tert*-Butyl(diphenylphosphanyl)amino-C-bis(trimethylsilyl)phosphaalkene (3a):** *t*Butylaminodiphenylphosphane **1a** (0.2565 g, 1 mmol) in 10 mL THF and LDA (0.5 mL of a 2 M solution in THF-heptane-ethylbenzene, 1 mmol) led to **2a** (δ = ^{31}P = 49.0 ppm), which reacted with 0.2245 g (1 mmol) of $(Me_3Si)_2C$=PCl to give 387 g (87 %) of **3a** as a brown oil. Single crystals of **3a** were obtained by storing a pentane solution at low temperature. **^{1}H NMR** (C_6D_6, 300 MHz): δ = 7.8–7–02 ppm (m, 10, Ph), 1.5 (s, 9 H, *t*Bu), 0.2 [d, 9 H, ^4J(P,H) = 2.6 Hz, $SiMe_3$], 0.0 (s, 9 H, $SiMe_3$). **^{13}C NMR** (C_6D_6, 75.46 MHz): δ = 189.5 [d, ^1J(P,C) = 97.7 Hz, C=P], 140.0 [D,D, ^1J(P,C) = 18.2, ^3J(P,C) = 2.6 Hz, *ipso*-C, Ph], 135.0 [d,d, ^2J(P,C) = 23, ^4J(P,C) = 4.8 Hz, *o*-C, Ph], 128.6 (s, *p*-C, Ph), 128.1 (d, ^3J(P,C) = 6.6 Hz, *m*-C, Ph), 59.4 [dd,, ^2J(P,C) = 23, ^2J(P,C) = 0.8 Hz, $C_{quart.}$ *t*Bu], 33.0 [d,d, ^3J(P,C) = 10.5, ^3J(P,C) = 4.1 Hz, CH_3 (*t*Bu)], 3.6 [d, ^3J(P,C) = 16.8 Hz, $SiMe_3$], 2.8 [d, ^3J(P,C) = 3.3 Hz, $SiMe_3$]. **^{31}P NMR** (C_6D_6, 121.5 MHz): δ = 372.9 [d, ^2J(P,P) = 11.5 Hz, P = C], 44.4 [d, ^2J(P,P) = 11.5 Hz, PPh_2]. ^{29}Si NMR (C_6D_6, 59.6 MHz): δ = –3.7 [d, ^2J(PSi) = 41.7 Hz], –10.1 [d, ^2J(PSi) = 10.6 Hz.]. **MS** (EI, 90 eV) *m*/*z* (%) = 445 (38) [M^+], 372 (100, M – $SiMe_3$), 316 (40, M – $SiMe_3$, –*t*Bu). $C_{23}H_{37}NP_2Si_2$ (M = 445.67 g·mol^{-1}): calcd. C 61.99, H 8.37, N 3.14 %; found C 61.72, H 8.01, N 3.40 %.

Selenium Addition to P-1-Adamantyl(diphenylphosphanyl)amino-C-bis(trimethylsilyl)phosphaalkene (3b): 3b was prepared as described.[8a] A solution of 0.673 g (1.28 mmol) **3b** in 5 mL CH_2Cl_2 was added dropwise to a suspension of grey selenium (0.253 g, 3.2 mmol) in 5 mL CH_2Cl_2. After 3 h ^{31}P NMR confirmed the complete consumption of **3b** in favor of *P*-1-adamantyl[diphenyl(selenoxo)phosphoranyl]amino-*C*-bis(trimethylsilyl)phosphaalkene {1-Ada[Ph_2P(=Se)]NP=C($SiMe_3$)$_2$, **3b=Se**}. Removal of unconsumed selenium by filtration and evaporation under high vacuum afforded a yellow solid (0.733 g, 95 %) containing **3b=Se**. Solutions of **3b=Se** in $CDCl_3$ contained, by ^{31}P NMR, about 10 % of the decomposition products 1-Ada[Ph_2P(= Se)]NH and [(Me_3Si)$_2$C=P]Se.[13]

3b=Se: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.9–7.24 (aryl multiplets), 2.46 [s, br., CH_2 (Ada)], 1.86 [br., CH (Ada)], 1.56 [m, CH_2 (Ada)], 0.37 (s, $SiMe_3$), 0.04 [d, ^3J(P,H) = 3.0 Hz, $SiMe_3$). **^{13}C NMR** ($CDCl_3$, 75 MHz): δ = 183.4 [d, d, ^1J(P,C) = 101.8, ^3J(P,C) = 4.6 Hz, C=P], 135.9 [d, d, ^1J(P,C) = 87.4, ^3J(P,C) = 1.8 Hz, *ipso*-C, Se = PPh_2], 133.8 [d, d, ^2J(P,C) = 10.9, ^4J(P,C) = 4.6 Hz, *o*-C, Se = PPh_2], 131.5 [d, ^4J(P,C) = 2.0 Hz, *p*-C, Se = PPh_2], 128.1 [d, ^3J(P,C) = 12.9 Hz, *m*-C, Se = PPh_2], 65.5 (s, br., C-P, Ada), 44.2 [pseudo-t, *N*(1–3) = 9.3 Hz, CH_2, Ada], 36.0 (s, CH_2, Ada), 30.1 (s, CH, Ada), 3.4 [d, ^3J(P,C) = 3.4 Hz, $SiMe_3$], 2.9 [d, ^3J(P,C) = 18.3 Hz, $SiMe_3$]. **^{31}P NMR** ($CDCl_3$, 121 MHz): δ = 350.4 (s, P=C), 45.7 [s, ^3J(SeP) = 742 Hz, Se=PPh_3]. **^{29}Si NMR** ($CDCl_3$, 59 MHz): δ = –4.4 [d, ^2J(PSi) = 45.2 Hz, –10.3 [d, ^2J(PSi) = 9.7 Hz] ppm. $C_{29}H_{43}NP_2SeSi_2$ (*M* = 602.16, exact mass 602.74): calcd. C 57.79, H 7.19, N 2.32 %; found C 57.79, H 7.32, N 2.45 %. **MS** (EI, 90 eV) *m*/*z* (%) = 415 (10, $Ph_2PSeNHAda^+$), 369 (36, $M^+ - Ph_2Se$), 73 (100, $SiMe_3^+$).

1-Ada[Ph_2P(=Se)]NH: ^{31}P NMR ($CDCl_3$, 121 MHz): δ = 44.8 [s, ^1J(SeP) = 752.1 Hz. ^{77}Se NMR ($CDCl_3$, 57 MHz): δ = –185.6 [d, ^1J(SeP) = 752.2 Hz] ppm. $C_{22}H_{26}NPSe$ (*M* = 414.38, exact mass 415.10): calcd. C 63.77, H 6.32, N 3.38 %; found C 63.12, H 6.11, N 3.35 %. **MS** (EI, 90 eV) *m*/*z* (%) = 415 (100) [M^+], 334 (36) [$M^+ - Se$].

***P*-(2,4,6-Tri-*tert*-butylphenyl)(diphenylphosphanyl)amino-C-bis(trimethylsilyl)phosphaalkene (3g):** 2,4,6-Tri-*tert*-butylphenylaminodiphenylphosphane (**1g**) (1.8 g, 4.05 mmol) in 10 mL THF reacted with an equimolar amount of LDA (2.1 mL of a 2 M solution in THF-heptane-ethylbenzene, 4.2 mmol) to give **2g** (δ = ^{31}P = 58.0 ppm), which in turn reacted with 0.9 g (4.05 mmol) (Me_3Si)$_2$C=PCl, furnishing **3g** (2.3 g, 90 %) as a yellowish solid. **^{1}H NMR** (C_6D_6, 300 MHz): δ = 8.04–6.95 (m, aromatic H), 1.65 [s,*o*-*t*Bu (Mes*)], 1.35 [s, *p*-*t*Bu (Mes*)], 0.62 [d, ^4J(P,H) = 3.5 Hz, $SiMe_3$], 0.0 (s, $SiMe_3$). **^{13}C NMR** (C_6D_6, 75.46 MHz): δ = 147.6 [d, ^3J(P,C) = 4.1 Hz, *o*-C (Mes*)], 147.6 (s, *p*-C, Mes*), 143.1 [d,d, ^2J(P,C) = 16.7 and 9.9 Hz, *ipso*-C (Mes*), 139.9 [d,d, ^1J(P,C) = 29.2, ^3J(P,C) = 6.9 Hz, *ipso*-C (PPh_2)],135.3 [d,d, ^2J(P,C) = 28.9, ^4J(P,C) = 8.3 Hz], 129.4 (s, *p*-C, PPh_2], 128.1 [d, ^3J(P,C) = 9.3 Hz, *m*-C, PPh_2], 126.8 [d, ^4J(P,C) = 2.3 Hz, *m*-C, Mes*], 37.9 [d, ^3J(P,C) = 0.9 Hz, *o*-C], 34.7 [t, line distance 2.6 Hz, CH_3 (*o*-*t*Bu, Mes*)], 34.5 [s, *p*-*t*Bu, $C_{quart.}$], 31.1 [s, CH_3, *p*-*t*Bu (Mes*)], 5.0 [d, ^3J(P,C) = 20.3 Hz, $SiMe_3$], 3.3 [d, ^3J(P,C) = 2.2 Hz, $SiMe_3$]. **^{31}P NMR** (C_6D_6, 121.5 MHz): δ = 337.7 [d, ^2J(P,P) = 21 Hz, P = C, I = ca. 1.5], 330.5 [d, ^2J(P,P) = 57.1 Hz, P = C, I = ca. 7], 74.0 [d, ^2J(P,P) = 57.1 Hz, PPh_2, I = ca. 13.5],], 55.1 [d, ^2J(P,P) = 20.9 Hz, PPh_2, I = ca. 2.6].$C_{37}H_{57}NP_2Si_2$ [*M* = 633.97 (exact mass 633.35)]. **MS** (EI, 90 eV) *m*/*z* (%): 633 (44) [M^+], 618 (35, $M^+ - CH_3$), 576 (20, $M^+ - t$Bu), 448 (64, $M^+ - PPh_2$), 388 (30, M^+ – Mes), 73 (100, $SiMe_3$).

***P*-(2,6-Diisopropylphenyl)(diphenylphosphanyl)amino-C-bis(trimethylsilyl)phosphaalkene (3h):** *P*-2,6-Diisopropylphenylaminodiphenylphosphane (**1h**) (2.5 g, 7.44 mmol) in 10 mL THF was metallated with an equimolar amount of *n*-butyllithium (2.5 M solution in hexane) leading to **2h** (δ = ^{31}P = 42.4 ppm). This reacted with 1.67 g (7.44 mmol) (Me_3Si)$_2$C=PCl delivering a yellow impure oil that contained, according to ^{31}P NMR, about 60 % of **3h**, 20 % of the starting material **1h**, and 20 % of *P*-2,6-diisopropylphenylamino-*C*-bis(trimethylsilyl)phosphaalkene. A few pale yellow crystals of **3h** were grown from a THF/pentane mixture. **^{31}P NMR** (C_6D_6, 81 MHz): δ = 335.8 (s, br., P=C), and 58.8 (s, br., PPh_2), **3h** (about 60 %), 316.5 (s, probably the DIPP-aminophosphaalkene, about 20 %), 42. 9 (s, **1h**, about 20 %).

***P*-*tert*-Butyl(diphenylphosphanyl)amino-C-bis(isopropyldimethylsilyl)phosphaalkene (4a):** *t*Butylaminodiphenylphosphane (**1a**) (1.20 g, 4.66 mmol) in 10 mL THF reacted with LDA (2.4 mL of a 2M solution in THF-heptane-ethylbenzene, 4.8 mmol) to give **2a** (δ = ^{31}P = 49.7 ppm), which in turn reacted with (iPrMe$_2$Si)$_2$C=PCl (1.31 g, 4.66 mmol), yielding 2.0 g (85 %) of **4a** as a brown viscous oil. For proposed ^{1}H and ^{13}C NMR assignments, see Scheme 5. **^{1}H NMR** (300 MHz, C_6D_6): δ = 7.66–7.60 (m, aryl H **i**), 7.13–6.97 (m, aryl H **k**, **j**), 1.46 (s, CH_3, **m**), 1.21–1.09 (m, C-H, **e**, **f**), 0.99 [d, ^5J(P,H) = 6.8 Hz, CH_3, **d**], 0.81 [d, ^5J(P,H) = 4.0 Hz, CH_3, **c**], 0.21 [d, ^4J(P,H) = 2.3 Hz, CH_3Si **b**], 0.0 ppm (s, CH_3Si **a**). **^{13}C NMR** (75.5 MHz, C_6D_6): δ = 179.1, (d, d-like X-part of AMX, *N* = 98.7 Hz and 6 Hz, P=C, **g**), 139.4 [d, ^1J(P,C) = 21.0 Hz, aryl-C, **h**], 134.1 [d, d-like X-part of AMX, *N* = 22.7 Hz and 3.6 Hz, aryl-C, **i**), 128.9 [d, ^3J(P,C) = 6.4 Hz, aryl-C, **j**], 128.3 (s, aryl *p*-C, **k**), 60.3 [d, d, ^2J(P,C) = 16.8 Hz and 1.6 Hz, N-C, **l**], 32.8 [d, d-like X-part of AMX, ^3J(P,C) = 8.4 Hz and 5.2 Hz, CH_3 (*t*Bu), **m**], 17.9 [s, CH_3 (*i*Pr), **c**], 17.8 [d, ^4J(P,C) = 2.2 Hz, CH_3 (*i*Pr), **d**], 15.4 [d, ^3J(P,C) = 12.6 Hz, CH (*i*Pr), **f**], 14.3 [s, CH (*i*Pr), **e**), –0.4 [d, ^2J(P,C) = 18.6, CH_3Si, **b**), –1.7 (s, CH_3Si, **a**). **^{29}Si NMR** (59.6 MHz, C_6D_6): δ = 1.8 [d, ^2J(PSi) = 35.2 Hz], –4.4 [d, ^2J(PSi) = 9.5 Hz]. **^{31}P NMR** (121.5 MHz, C_6D_6): δ = 382.3 (d) and 47.0 [d, ^2J(P,P) = 6.6 Hz]. $C_{27}H_{45}NP_2Si_2$ (M = 501.77; exact mass 501.26 g.mol^{-1}): calcd. C 64.63, H 9.04, N 2.79 %; found C 62.99, H 8.95, N 2.70 %. **MS** (EI, 90 eV) *m*/*z* (%); 501 (4) [M^+], 400 (100, $M^+ - i$PrMe$_2$Si), 344 (16, $M^+ - i$PrMe$_2$Si, – C_4H_8).

***P*-1-Adamantyl(diphenylphosphanyl)amino-C-bis(isopropyldimethylsilyl)phosphaalkene (4b):** 1-Adamantylaminodiphenylphosphane (**1b**) (0.93 g, 2.76 mmol) in 10 mL THF reacted with LDA (1.4 mL of a 2 *M* solution in THF-heptane-ethylbenzene, 2.8 mmol) to give **2b** (δ = ^{31}P = 45.3 ppm), which in turn reacted with (iPrMe$_2$Si)$_2$C=PCl (0.78 g, 2.76 mmol), yielding 1.3 g (82 %) of **4b** as a yellow solid, m.p. 97–98 °C. Recrystallization from hexane at –20 °C gave yellow crystals suitable for X-ray diffraction. **^{1}H NMR** (300 MHz, C_6D_6): δ = 7.73–7.68 (m, aryl H **i**), 7.10–6.94 (m, aryl H **k**, **j**), 1.92 (s, Ada,), 1.51–1.39 (m, Ada,), 1.13–0.95 (m, Ada), 1.13–0.95 (m, C-H, **c**, **e**, **f**), 0.83 [d, ^5J(P,H) = 7.2 Hz, CH_3, **d**], 0.20 [d, ^4J(P,H) = 2.5 Hz, CH_3Si **b**), 0.0 ppm (s, CH_3Si **a**). **^{13}C NMR** (75.5 MHz, C_6D_6): δ = 183.7, (d, ^1J = 102.6 Hz, P = C, **g**), 139.8 [d, d-like X-part of AMX, ^2J(P,C) = 19.1, ^4J(P,C) = 2.5 Hz, aryl-C, **h**], 134.6 [d, d-like X-part of AMX, ^2J(P,C) = 22.9, ^4J(P,C) = 4.5 Hz, aryl-C, **i**], 128.2 (s, aryl *p*-C, **k**), 127.8 [d, ^3J(P,C) = 6.5 Hz, aryl-C, **j**], 61.1 [d, ^2J (PC) = 19.6 Hz, N-C, **l**], 45.8 [d, d-like X-part of AMX, ^3J = 10.7 Hz and 4.0 Hz, Ada], 36.3 (s, Ada), 30.9 (s, Ada), 18.0 [s, CH_3 (*i*Pr), **c**], 17.8 [d, ^4J(P,C) = 2.8 Hz, CH_3 (*i*Pr), **d**], 15.5 [d, ^3J(P,C) = 13.6 Hz, CH (*i*Pr), **f**], 14.6 [s, CH (*i*Pr), **e**], –0.3 [d, ^2J(P,C) = 17.8, CH_3Si, **b**], –1.6 (s, CH_3Si, **a**). **^{29}Si NMR** (59.6 MHz, C_6D_6): δ = 1.5 [d, ^2J(PSi) = 36.0 Hz], –4.7 [d, ^2J(PSi) = 9.7 Hz]. **^{31}P NMR** (121.5 MHz, C_6D_6): δ = 385.7 (d) and 38.3 [d, ^2J(P,P) = 10.0 Hz] ppm. $C_{33}H_{51}NP_2Si_2$ (*M* = 579.99, exact mass = 359.30 g·mol^{-1}): calcd. C 68.35, H 8.86, N 2.42 %; found C

66.51, H 8.80, N 2.45 %. **MS** (EI, 90eV) *m/z* (%) = 579 (4) [M^+], 564 (2, $M^+ - CH_3$), 478 (100, $M^+ - i$PrMe$_2$Si).

***P*-Isopropyl(diphenylphosphanyl)amino-C-bis(isopropyldimethylsilyl)phosphaalkene (4c):** Isopropylaminodiphenylphosphane (**1c**) (1.04 g, 4.26 mmol) in 10 mL THF reacted with LDA (2.2 mL of a 2 M solution in THF-heptane-ethylbenzene, 4.4 mmol) to give **2c** (δ = ^{31}P = 41.9 ppm), which in turn reacted with (iPrMe$_2$Si)$_2$C=PCl (1.2 g, 4.26 mmol), yielding 1.77 g (86 %) of **4c** as a brown viscous oil. **^{1}H NMR** (300 MHz, C_6D_6): δ = 7.30–7.23 (m, aryl H **i**), 6.94–6.82 (m, aryl H **k**, **j**), 4.12–3.97 (m, *i*Pr-N), 1.31–1.22 (m, *i*Pr), 1.03 [d, J(P,H) = 6.6 Hz, *i*Pr], 0.76 [d, J(P,H) = 7.6 Hz, *i*Pr], 0.08 (s, CH_3Si **a**), - 0.01 [d, ^4J(P,H) = 3.7 Hz, CH_3Si **b**]. **^{13}C NMR** (75.5 MHz, C_6D_6): δ = 144.3, [d, d-like X-part of AMX, ^1J(P,C) = 91.0, ^3J(P,C) = 4.6 Hz, P = C, **g**], 139.3 [d, d-like X-part of AMX, ^1J(P,C) = 18.3, ^2J(P,C) = 4.6 Hz, aryl-C, **h**], 132.5 [d, d-like X-part of AMX, ^2J(P,C) = 21.4, ^4J(P,C) = 2.4 Hz, aryl-C, **i**], 128.6 (s, aryl *p*-C, **k**), 128.6 [d, ^3J(P,C) = 6.1 Hz, aryl-C, **j**], 53.0 [d, ^2J (PC) = 13.6 Hz, N-C, **l**], 24.5 [d, d-like X-part of AMX, ^3J(P,C) = 8.9 Hz and 5.2 Hz, CH_3 (*i*Pr-N), **m**], 17.8 [s, CH_3 (*i*Pr), **c**], 17.7 [d, ^4J(P,C) = 2.2 Hz, CH_3 (*i*Pr), **d**], 15.2 [d, ^3J(P,C) = 10.2 Hz, CH (*i*Pr), **f**], 13.9 [d, d-like X-part of AMX, J = 5.7 Hz and 2.1 Hz, CH (*i*Pr), **e**], –0.4 (s, CH_3Si, **a**), –0.6 [d, ^2J(P,C) = 18.6, CH_3Si, **b**]. **^{29}Si NMR** (59.6 MHz, C_6D_6): δ = 3.1 [d, ^2J(PSi) = 40.1 Hz], –5.6 [d, ^2J(PSi) = 10.7 Hz]. **^{31}P NMR** (121.5 MHz, C_6D_6): δ = 343 [d, ^2J(P,P) = 13.8 Hz, P = C], 44 [br., ^2J(P,P) not resolved, PPh_2] ppm.

***P*-Triphenylmethyl(diphenylphosphanyl)amino-C-bis(isopropyldimethylsilyl)phosphaalkene (4d):** Triphenylmethylaminodiphenylphosphane **1d** (0.52 g, 1.17 mmol) in 10 mL THF reacted with LDA (0.6 mL of a 2 *M* solution in THF-heptane-ethylbenzene, 1.2 mmol) to give **2d** (δ = ^{31}P = 53.5 ppm), which in turn reacted with (iPrMe$_2$Si)$_2$C=PCl (0.33 g, 1.17 mmol), yielding a yellowish oil. According to ^{31}P NMR (two sets of AX patterns) this contains two phosphanylamino phosphaalkene species (about 60 % and 35 % of the signal intensity), accompanied by small amounts of the aminophosphaalkene (iPrMe$_2$Si)$_2$C=PN(H)CPh$_3$ [δ = ^{31}P = 317.6 ppm (s); pure sample: δ = 318 ppm][8] and of the aminophosphane **1d** [δ = ^{31}P = 27.5 ppm (s)]. Purification of **4d** was not achieved. **^{31}P NMR** (C_6D_6, 81 MHz): **4d**: δ = 366.5 [d, ^2J(P,P) = 32.8 Hz], 361.5 [d, ^2J(P,P) = 40.0 Hz], 25.6 ppm [d, ^2J(P,P) = 32.8 Hz], 15.4 ppm [d, ^2J(P,P) = 40.0 Hz].

***P*-Phenyl(diphenylphosphanyl)amino-C-bis(isopropyldimethylsilyl)phosphaalkene (4e):** Phenylaminodiphenylphosphane (**1e**) (1.87 g, 6.75 mmol) in 10 mL THF reacted with LDA (1.4 mL of a 2 M solution in THF-heptane-ethylbenzene, 2.8 mmol) to give **2e** (δ = ^{31}P = 38.2 ppm), which in turn reacted with (iPrMe$_2$Si)$_2$C=PCl (1.9 g, 6.75 mmol) to yield **4e** (2.94 g, 84 %) as a yellow solid (m.p. 81–82 °C). **^{1}H NMR** (300 MHz, C_6D_6): δ = 7.74–6.85 (m, several multiplets from aryl protons), 1.09–0.94 (m, C-H, *i*Pr, **c**, **d, e**, **f**, **d**), 0.38 [d, ^4J(P,H) = 3.6 Hz, CH_3Si **b**), 0.0 ppm (s, CH_3Si **a**). **^{13}C NMR** (75.5 MHz, C_6D_6): δ = 163.8, (d, d-like X-part of AMX, ^1J(P,C) = 93, ^3J(P,C) = 7.5 Hz, **g**), 150.5 (d, d-like X-part of AMX, J(P,C) = 10.7 and 5.7 Hz, aryl-C, **l**), 138.4 (d, d-like X-part of AMX, J(P,C) = 19.9 and 5.4 Hz, **h**), 133.8 (d, d-like X-part of AMX, J(P,C) = 21.5 and 2.8, **i**), 129.6 [d, J(P,C) = 10.5 Hz, aryl-C], 128.9 [d, J(P,C) = 6.5 Hz, aryl-C, **j**], 127.1 (d, d-like X-part of AMX, N = 7.1 and 1.6 Hz, aryl-C), 124.8 [d, J(P,C) = 1.6 Hz, aryl-C], 18.34 [s, CH_3 (*i*Pr), **c**], 18.3 [s, CH_3 (*i*Pr), **d**], 15.5 [d, ^3J(P,C) = 9.4 Hz, CH (*i*Pr), **f**], 13.2 [s, CH (*i*Pr), **e**), –0.5 [d, ^2J(P,C) = 20.9, CH_3Si, **b**), –1.9 (s, CH_3Si, **a**). **^{29}Si NMR** (59.6 MHz, C_6D_6): δ = 2.3 [d, ^2J(PSi) = 38.2 Hz], –4.6 [d, ^2J(PSi) = 9.4 Hz]. **^{29}Si NMR** (59.6 MHz, C_6D_6): δ = [ppm] = 2.3 [d, ^2J(PSi) = 38.2 Hz], –4.6 [d, ^2J(PSi) = 9.4 Hz]. **^{31}P NMR** (81 MHz, C_6D_6): δ = 351.3 [d, ^2J(P,P) = 67.5 Hz], 60.9 [d, ^2J(P,P) = 67.5 Hz]. $C_{29}H_{41}NP_2Si_2$ (M = 521.76, exact mass = 521.23): calcd. C 66.76, H 7.92, N 2.68 %; found C 65.78, H 7.92, N 2.99 %. **MS** (EI, 90 eV) *m/z* (%): 521 (7) [M^+], 506 (2, $M^+ - CH_3$), 478 (3, $M^+ - i$Pr), 420 (100, M^+. iPrMe$_2$Si).

***P*-2,4,6-Trimethylphenyl(diphenylphosphanyl)amino-C-bis(isopropyldimethylsilyl)phosphaalkene (4f):** 2,4,6-Trimethylphenylaminodiphenylphosphane **1f** (0.68 g, 2.14 mmol) in 10 mL THF reacted with LDA (1.1 mL of a 2 M solution in THF-heptane-ethylbenzene, 2.2 mmol) to give **2e** (δ = ^{31}P = 49.9 ppm), which in turn reacted with (iPrMe$_2$Si)$_2$C=PCl (0.6 g, 2.14 mmol), forming, according to $^{31\prime}$P NMR, **4f** as the main product and the starting material **1f** (δ = ^{31}P = 36.5 ppm) as impurity. The attempted purification of **4f** failed since increasing amounts of **1f** were observed. **4f**: **^{31}P NMR** (C_6D_6, 81 MHz) δ = 331 ppm and 64 ppm [broad signals, ^2J(P,P) not resolved].

***P*-(2,4,6-Tri-tert-butylphenyl)(diphenylphosphanyl)amino-C-bis(isopropyldimethylsilyl)phosphaalkene (4g):** 2,4,6-Tri-tert-butylphenylaminodiphenylphosphane (**1g**) (1.58 g, 3.54 mmol) in 10 mL THF reacted with an equimolar amount of LDA (1.8 mL of a 2M solution in THF-heptane-ethylbenzene, 3.6 mmol) to give **2g** (δ = ^{31}P = 58.3 ppm). This in turn reacted with (iPrMe$_2$Si)$_2$C=PCl (1.0 g, 3.54 mmol) to form **4g** as a mixture of isomers (conformers) also containing the aminophosphaalkene (iPrMe$_2$Si)$_2$C=PN(Mes*)PPh_2 (δ = ^{31}P = 325 ppm).[8] One of the isomers of **4g** was crystallized from a mixture of hexane and acetonitrile at –20 °C, but NMR spectroscopic data could not be determined because of the small amount of crystals. **4g** (mixture of rotamers): **^{31}P NMR** (81 MHz, C_6D_6): δ = 341.2 and 72.6 [d, ^2J(P,P) = 67.5 Hz, about 60 % signal intensity], 337.8 and 50.2 [d, ^2J(P,P) = 67.5 Hz, about 40 % signal intensity]. **MS** (EI, 90 eV) *m/z* (%) 689 (2.2) [M^+], 674 (6.8, $M^+ - CH_3$), 646 (12, $M^+ - C_3H_7$), 444 (42, M^+ – Mes*).

X-ray Crystallography: Crystal data are summarized in Table 3 and Table 4. Crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of an Oxford Diffraction Xcalibur A or (for **3h**) Nova E diffractometer. Intensity measurements were performed using monochromated Mo-K_α radiation or (for **3h**) mirror-focussed Cu-K_α radiation, respectively. Absorption corrections were based on multi-scans. Structures were refined anisotropically on F^2 using the program SHELXL-97.[14] All NH hydrogens were refined freely; other hydrogen atoms were included using a riding model or rigid methyl groups. *Exceptions and special features*: Compound **3g** crystallizes in $P2_12_12_1$, but the symmetry is close to *Pnma*. The structure was refined as an enantiomeric twin, with a Flack parameter of 0.22(4). For compound **4g**, the SiMe$_2$*i*Pr group Si2, C6–10 was disordered over two positions with relative occupations 0.835, 0.165(2). Appropriate similarity restraints were used to improve refinement stability, but the dimensions of disordered groups should be interpreted with caution.

We reported the structure of compound **3b** in a short communication, CCDC-731434.[3] Herein it is discussed in detail for the first time.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1055077 (**1b**), CCDC-1055311 (**1f**), CCDC-1055310 [**1f**(P=O)], CCDC-1054304 (**3a**), CCDC-1054305 (**3g**), CCDC-1054302 (**3h**), CCDC-1055308 (**4b**), and CCDC-1055309 (**4g**). (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Table 3. X-ray crystallographic details for **1b**, **1f**, **1f**(P=O), and **3a**.

	1b	**1f**	**1f**(P=O)	**3a**
Chemical formula	$C_{22}H_{26}NP$	$C_{21}H_{22}NP$	$C_{21}H_{22}NOP$	$C_{23}H_{37}NP_2Si_2$
M_r	335.41	319.37	335.37	445.66
Crystal system	triclinic	monoclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Temperature /K	100	100	100	100
a /Å	7.5097(3)	15.3841(3)	9.5330(6)	9.9254(2)
b /Å	11.1582(5)	4.61047(8)	10.1794(8)	10.0539(3)
c /Å	12.2429(5)	25.9647(4)	20.0680(10)	14.7695(2)
α /°	101.028(3)	90	76.972(4)	72.141(2)
β /°	105.671(3)	107.566(2)	77.500(4)	80.766(2)
γ /°	107.589(5)	90	70.086(6)	67.700(3)
V /Å^3	898.99	1755.75	1763.0	1296.27
d_{calc} /g·cm^{-3}	1.239	1.208	1.264	1.142
Z	2	4	4	2
$F(000)$	360	680	712	480
μ /mm^{-1}	0.16	0.16	0.16	0.27
Crystal size /mm	0.10 × 0.09 × 0.07	0.26 × 0.23 × 0.19	0.14 × 0.13 × 0.06	0.16 × 0.14 × 0.11
Transmissions	No abs. corr.	0.96–1.00	0.99–1.00	0.97–1.00
$2\theta_{max}$ /°	52.7 (Mo-K_α)	56.6 (Mo-K_α)	52.7 (Mo-K_α)	56.6 (Mo-K_α)
No. of measured and independent reflections	21740, 3675	54206, 4342	46268, 7201	25526, 5977
R_{int}	0.040	0.025	0.062	0.032
$wR(F^2)$ all refl., R_1 [$F > 4\sigma(F)$]	0.062, 0.033	0.097, 0.034	0.085, 0.040	0.077, 0.031
S(F^2)	0.88	1.07	0.82	0.95
No. of parameters / restraints	221 / 0	215 / 0	447 / 0	262 / 0
$\Delta\rho_{max, min}$ /e·Å^{-3}	0.29, –0.31	0.45, –0.21	0.33, –0.36	0.48, –0.20

Table 4. X-ray crystallographic details for **3g**, **3h**, **4b** and **4g**.

	3g	**3h**	**4b**	**4g**
Chemical formula	$C_{37}H_{57}NP_2Si_2$	$C_{31}H_{45}NP_2Si_2$	$C_{33}H_{51}NP_2Si_2$	$C_{41}H_{65}NP_2Si_2$
M_r	633.96	549.80	579.87	690.06
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$P2_1/c$
Temperature /K	100	100	100	100
a /Å	11.2381(2)	8.6563(2)	10.3169(4)	21.9125(4)
b /Å	15.7876(2)	18.6668(2)	33.8246(6)	15.8146(2)
c /Å	21.0360(2)	20.1109(4)	10.6425(4)	11.9245(2)
α /°	90	90	90	90
β /°	90	98.159(2)	118.456(4)	95.475(2)
γ /°	90	90	90	90
V /Å^3	3732.26	3216.74	3262.38	4115.12
d_{calc} /g·cm^{-3}	1.128	1.135	1.181	1.114
Z	4	4	4	4
$F(000)$	1376	1184	1256	1504
μ /mm^{-1}	0.21	2.1	0.23	0.19
Crystal size /mm	0.27 × 0.23 × 0.22	0.18 × 0.15 × 0.15	0.25 × 0.13 × 0.12	0.35 × 0.30 × 0.15
Transmissions	0.98–1.00	0.66–1.00	0.99–1.00	0.96–1.00
$2\theta_{max}$ /°	58.4 (Mo-K_α)	152 (Cu-K_α)	56.6 (Mo-K_α)	56.6 (Mo-K_α)
No. of measured and independent reflections	76591, 9265	36226, 6595	84436, 8086	135264, 10180
R_{int}	0.024	0.032	0.036	0.037
$wR(F^2)$ all refl., R_1 [$F > 4\sigma(F)$]	0.071, 0.026	0.094, 0.034	0.079, 0.030	0.081, 0.030
S(F^2)	1.00	1.04	0.99	1.02
No. of parameters / restraints	395 / 0	335 / 0	351 / 0	457 / 102
$\Delta\rho_{max, min}$ /e·Å^{-3}	0.28, –0.19	0.34, –0.30	0.41, –0.18	0.35, –0.26

Supporting Information (see footnote on the first page of this article): contains the structures of **1b**, **1f**, and of **1f(P=O)** (Figs. S1 – S3) as well as a consideration of conformational influences on ^2J(PP) (Scheme S1).

Keywords: Phosphaalkenes; Phosphane ligands; Iminophosphanes; π-interaction; Conformational analysis

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