Inversely Polarized Phosphaalkenes as Phosphinidene- and Carbene-Transfer Reagents

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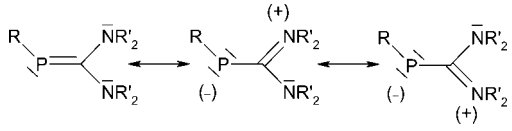
The reaction of the inversely polarized phosphaalkenes $RP=C(NMe_2)_2$ [R = *t*Bu (**1a**), Cy (**1b**), 1-Ad (**1c**), Ph (**1d**), Mes (**1e**)] with an excess of diphenyl ketene in *n*-pentane affords the zwitterionic adduct $(Me_2N)_2C–C(O)=CPh_2$ (**2**) and the 3,5-dibenzhydrylidene-1,4,2-dioxaphospholanes **4a**–**e**. The reaction of **1a** with $Ph_2C=C=O$ in concentrated acetonitrile solution gives **4a** and 5-benzhydrylidene-2-*tert*-butyl-4,4-diphenyl-1,2-oxaphospholan-3-one (**6a**) as a by-product. In contrast, treatment of $Me_3SiP=C(NMe_2)_2$ (**1i**) with the ketene leads to the formation of 2-phospha-1,3-butadiene (**5**). The thermolabile phosphaalkene **8** decomposes into an imidazolylidene and (*t*BuP), the latter species spontaneously oligomerizes to $(tBuP)_n$ (n = 3, 4). Obviously, compounds **1a**–**e** serve as a convenient source of phosphinidenes and the carbene $C(NMe_2)_2$. A Wanzlick-type equilibrium between these species, however, must be excluded according to exchange and cross-coupling experiments. The molecular structures of **2**, **4e** and **6a** were determined by X-ray structure analyses.

Introduction

The phosphorus atom of inversely polarized phosphaalkenes such as $R–P=C(NR'_2)_2$ (R = H, alkyl, aryl, $SiMe_3$, R′ = Me, Et) is highly nucleophilic, which is rationalized by an effective π-electron delocalization of the lone pairs at the trigonal-planar amino substituents into the P–C multiple bond (Scheme 1).[1]

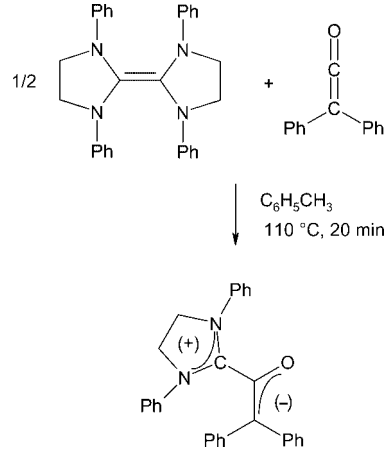


Scheme 1. Limiting formulae of amino-substituted phosphaalkenes.

Protonation,[2] alkylation,[2,3] silylation,[3] and coordination to metal centers occur at the P atom with increase of the coordination number.[2,4,5] Treatment of $tBuP=C(NMe_2)_2$ with [$(Ph_3P)AuCl$], for example, leads to the cleavage of the P–C bond of some of the phosphaalkene units to yield phosphanediide units [$tBuP^{2-}$], which are incorporated as ligands in the decanuclear cluster cation $[Au_8(AuCl)_2(\mu^3\text{-}PtBu)_2\{tBuP=C(NMe_2)_2\}_6]^{4+}$. The carbodiimmonium dication $[Me_2N=C=NMe_2]^{2+}$ formed as a by-product has been trapped by chloride to afford the spectroscopically detected chloroformamidinium ion $[(Me_2N)_2CCl]^+$.[6] This transformation is formally related to the synthetic pathway to carbene complexes of transition metals via the C=C bond cleavage of bis(imidazol-2-ylidenes) in the coordination sphere of a metal atom.[7]

The conceivable dissociation of tetraamino-substituted alkenes into carbenes was already postulated by Wanzlick in the 1960s.[8] However, the ^1H NMR spectroscopic proof of Wanzlick's ideas was only provided by Hahn some 40 years later.[9]

In line with the diagonal relationship in the periodic table between the elements carbon and phosphorus, the quest for a Wanzlick-type reaction of the electron-abundant bis(amino)phosphaalkenes seems intriguing as, in addition to a relatively stable bis(amino)carbene,[10] the homolytic cleavage of the phosphaalkene would furnish reactive phosphin-



Scheme 2. Formation of a carbene/ketene adduct.

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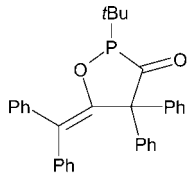
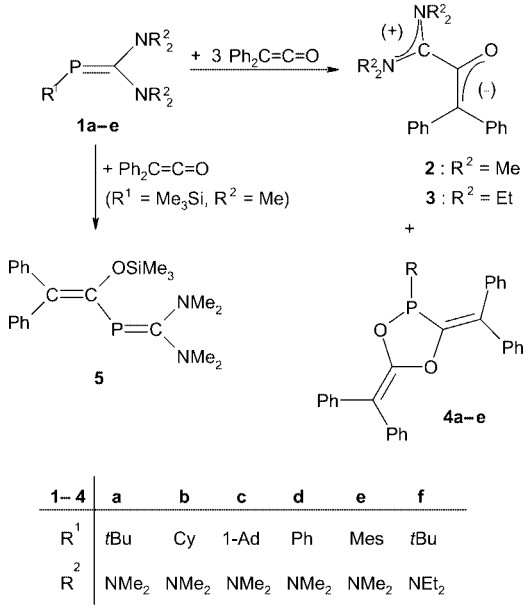
idene fragments under relatively mild conditions. For our work, the reaction of 1,1′,3,3′-tetraphenyl-2,2′-bis(imidazolidinylidene) with diphenyl ketene by Regitz et al. serves as a model reaction for the trapping of a carbene produced in agreement with Wanzlick's postulate[11] (Scheme 2).



6a

Results and Discussion

Reaction of the phosphaalkenes R–P=C(NMe_2)$_2$ [**1a**–**e**; R = *t*Bu (**1a**),Cy = *c*C_6H_{11} (**1b**), 1-Ad (**1c**), Ph (**1d**), Mes (**1e**)] with an excess of diphenyl ketene in pentane at 0–20 °C for 16 h led to the precipitation of the light-yellow zwitterionic compound **2** in about 85% yield. The product was purified by chromatography on a silica column. After removal of **2**, the mother liquor was treated with an excess of powdered NaOH to destroy the excess of ketene. Filtration and concentration of the filtrate to dryness gave 3,5-dibenzhydrylidene-1,4,2-dioxaphospholanes **4a**–**e** as colorless waxy solids in 45–53% yield. Purification of these products was accompanied by decomposition (Scheme 3).



1–4	a	b	c	d	e	f
R^1	*t*Bu	Cy	1-Ad	Ph	Mes	*t*Bu
R^2	NMe_2	NMe_2	NMe_2	NMe_2	NMe_2	NEt_2

Scheme 3. Formation of compounds **2**, **3**, **4a**–**e**, and **5**.

The reactions between **1a**–**e** and diphenyl ketene were also performed in acetonitrile. Treatment of concentrated solutions of the phosphaalkene in acetonitrile (ca. 20% v/v) with neat Ph_2C=C=O gave rise to the instantaneous formation of dark-violet emulsions and generation of heat. From NMR evidence it was clear that the same products **2** and **4a**–**e** were generated as previously in pentane solution. Workup, however, did not afford pure compounds. In the case of *t*BuP=C(NMe_2)$_2$ a few crystals of 5-benzhydrylidene-2-*tert*-butyl-4,4-diphenyl-1,2-oxaphospholan-3-one (**6a**) were isolated as a by-product. This species is isomeric to **4a** and has also to be considered as the formal result of the cyclization of 2 equiv. of ketene with *tert*-butyl-phosphinidene.

Analogously to the behavior of **1a**, *t*BuP=C(NEt_2)$_2$ (**1f**) and an excess of diphenyl ketene in pentane underwent reaction to yield yellow solid **3** (73%) in addition to **4a** (Scheme 3).

The reactions under discussion are the first examples where phosphaalkenes serve as convenient sources of carbenes as well as phosphinidenes. The use of this synthetic principle, however, is limited. Thus, treatment of phosphaalkene HP=C(NMe_2)$_2$ (**1g**) with diphenyl ketene under comparable conditions led to complete decomposition of the reagents, and no reaction occurred between the ketene and the sterically encumbered compound Mes*P=C(NMe_2)$_2$ (**1h**). The behavior of Me_3SiP=C(NMe_2)$_2$ (**1i**) towards diphenyl ketene is different from that of **1a**–**f**. Here, the carbonyl group of the ketene is inserted into the P–Si bond of **1h** with the formation of the 2-phospha-1,3-butadiene **5**. This thermolabile product was identified by spectroscopy without prior purification (Scheme 3).

This process parallels the reaction of **1i** with Me_3SiCH=C=O, where 1,1-bis(dimethylamino)-3-trimethylsiloxy-4-trimethylsilyl-2-phosphabutadiene ($\delta_{^{31}P}$ = 30.0 ppm) was obtained. Obviously, the reactivity of the P–Si bond in **1i** precludes the cleavage of the P=C bond of the phosphaalkene.[12]

The ^{1}H NMR spectrum of **2** shows two singlets at δ = 2.74 and 3.21 ppm of equal intensity, which are assigned to the protons of chemically and magnetically different dimethylamino groups. Resonances in the $^{13}C\{^1H\}$ NMR spectra at δ = 42.3 and 42.6 ppm also correspond to these groups. The singlets at δ = 141.6 and 175.4 ppm are caused by the carbon atom of the carbenium unit and by that of the carbonyl group. Two intense bands at $\tilde{\nu}$ = 1713 and 1613 cm^{-1} in the IR spectrum of the adduct can be assigned to the coupled CO and C=C stretching modes.

The $^{31}P\{^1H\}$ NMR spectra of the 1,4,2-dioxaphospholanes **4a**–**e** show singlets at δ = 90.6–122.3 ppm, in the region typical for (alkyl/aryl)(alkoxy)phosphanes. The resonances in the precursors **1a**–**e** are encountered at considerably higher field (δ = 9–91 ppm). The phosphorus atom in 2-phosphabutadiene (**5**) gives rise to a singlet at δ = 17.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum.

X-ray Structural Analysis of 2

To confirm the spectroscopic evidence for the adduct formation between carbene [$(Me_2N)_2$C] and diphenyl ketene, an X-ray structural analysis of **2** was performed (Figure 1, Table 1).

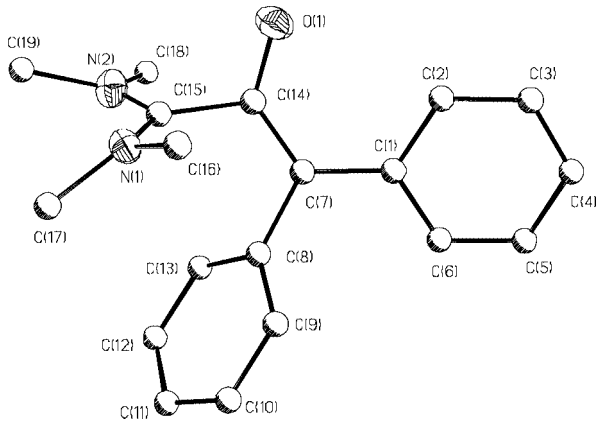


Figure 1. Molecular structure of **2** in the crystal. Selected bond lengths [Å] and angles [°]: N(1)–C(15) 1.336(10), N(1)–C(16) 1.480(10), N(1)–C(17) 1.463(10), N(2)–C(15) 1.325(10), N(2)–C(18) 1.471(10), N(2)–C(19) 1.480(10), C(14)–C(15) 1.516(11), O(1)–C(14) 1.295(9), C(7)–C(14) 1.372(11), C(7)–C(8) 1.502(11), C(1)–C(7) 1.461(11); C(16)–N(1)–C(17) 113.5(6), C(15)–N(1)–C(16) 121.3(6), C(15)–N(1)–C(17) 123.5(7), C(15)–N(2)–C(18) 121.3(7), C(15)–N(2)–C(19) 123.9(7), C(18)–N(2)–C(19) 114.6(7), N(1)–C(15)–C(14) 118.1(8), N(2)–C(15)–C(14) 119.5(7), N(1)–C(15)–N(2) 122.1(7), C(7)–C(14)–C(15) 117.6(8), O(1)–C(14)–C(15) 113.0(7), O(1)–C(14)–C(7) 129.3(7), C(14)–C(7)–C(8) 116.6(7), C(1)–C(7)–C(8) 118.9(7), C(1)–C(7)–C(14) 124.5(8).

Single crystals of **2** were grown from a CH_2Cl_2 solution at +4 °C. The analysis confirms the presence of a planar carbenium center, the positive charge of which is stabilized by π-conjugation with the two planar amino group [sum of angles at N(1) = 358.3°; N(2) = 359.8°]. In keeping with this, relatively short N(1)–C(15) [1.336(10) Å] and N(2)–C(15) [1.325(10) Å] bonds are also observed. The single bonds between the N atom and the methyl groups − N(1)–C(16) and N(1)–C(19) − are markedly longer [1.463(10)–1.480(10) Å]. The trigonal-planar configured atom C(15) (sum of angles 359.7°) is connected to the ketene part of the adduct by a C–C single bond of 1.516(11) Å. The C(14)–O(1) bond length of 1.295(9) Å clearly exceeds that of a localized carbonyl group (ca. 1.23 Å). This points to π-delocalization within the enolate part of the molecule, which means that the atoms C(14) (sum of angles 359.9°) and C(7) (sum of angles 360.0°) are trigonal-planar. The aryl ring C(1) to C(6) and the plane defined by the atoms O(1), C(14), C815), and C(7) form a dihedral angle of 22.2°. This plane forms an angle of 65.2° with the plane of the carbenium part defined by the atoms N(1), N(2), and C(15). The second aryl ring at C(7) is also twisted by 57.7° out of the plane of the atoms O(1), C(14), and C(7).

X-ray Structural Analysis of 4e

The constitution and configuration of the 3,5-dibenzhydrylidene-1,4,2-dioxaphospholanes **4a**–**c** and **4e** were also confirmed by X-ray structural analyses. Single crystals of **4a**–**c** and **4e** were grown from CH_2Cl_2 at +4 °C. As no significant differences were observed between the five-membered heterocycle of these compounds, only the structure of **4e** (R = Mes) is discussed here (Figure 2, Table 1).

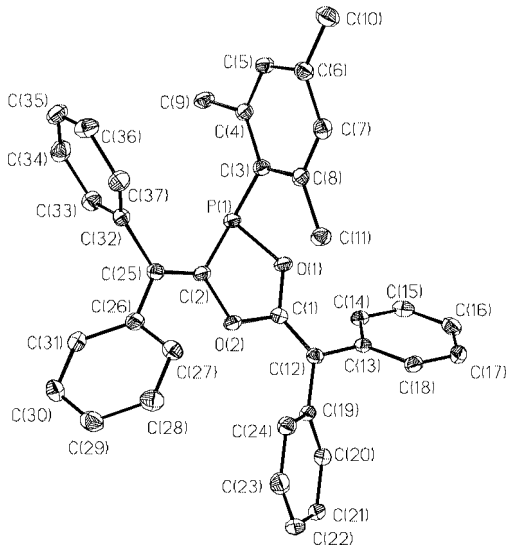


Figure 2. Molecular structure of **4e** in the crystal. Selected bond lengths [Å] and angles [°]: P(1)–C(2) 1.833(1), P(1)–C(3) 1.835(1), P(1)–O(1) 1.696(1), O(1)–C(1) 1.370(2), O(2)–C(1) 1.370(2), O(2)–C(2) 1.394(2), C(2)–C(25) 1.333(2), C(25)–C(26) 1.490(2), C(25)–C(32) 1.495(2), C(1)–C(12) 1.343(2), C(12)–C(13) 1.492(2), C(12)–C(19) 1.495(2); C(2)–P(1)–C(3) 104.22(6), O(1)–P(1)–C(3) 105.22(5), O(1)–P(1)–C(2) 88.08(5), P(1)–O(1)–C(1) 115.73(8), O(1)–C(1)–O(2) 112.59(1), C(1)–O(2)–C(2) 113.55(19), P(1)–C(2)–O(2) 109.40(10), P(1)–C(2)–C(25) 120.69(11), P(1)–C(2)–C(25) 129.86(10), O(1)–C(1)–C(12) 124.67(11), O(2)–C(1)–C(12) 122.73(11).

The key structural feature is the almost planar five-membered heterocycle (the largest deviation from the best plane is 0.0423 Å). The sum of the endocyclic angles is 539.35°, which is close to the theoretical value of 540°. The P(1)–O(1) bond [1.696(1) Å] is slightly shorter than the sum of the covalent radii of P (1.10 Å) and O (O.66 Å).[13] The endocyclic P(1)–C(2) bond [1.833(1) Å] is equally long as the exocyclic distance P(1)–C(3) [1.835(1) Å] to the mesityl substituent. The same is true for the endocyclic bond lengths C(1)–O(2) [1.370(2) Å] and C(2)–O(2) [1.394(2) Å]. All of them have a bond order of one. The exocyclic bonds C(1)–C(12) [1.343(2) Å] and C(2)–C(25) [1.333(2) Å] are double bonds. The phosphorus atom has a trigonal-pyramidal configuration (sum of angles = 297.52°). The P(1)–C(3) vector and the best plane of the heterocycle enclose an angle of 114.2°.

X-ray Structural Analysis of 6a

Yellow single crystals of **6a**, which is an isomer of **4a**, were grown from a saturated acetonitrile solution at ambient temperature (Figure 3, Table 1). The X-ray analysis revealed the molecule as a puckered 1,2-oxaphospholan-3-one (sum of angles = 530.53°). The trigonal-pyramidal phosphorus atom P(1) (sum of angles = 294.29°) forms P(1)–C(1) [1.869(2) Å], P(1)–O(1) [1.664(1) Å], and P(1)–C(5) [1.861(1) Å] single bonds to the neighboring atoms. The trigonal-planar C(5) atom is part of a carbonyl group [C(5)–O(2) = 1.206(2) Å]. The endocyclic bond O(1)–C(19)

of 1.406(2) Å is comparable to the C–O bonds in **4e** [1.394(2) and 1.370(2) Å]. The endocyclic C–C bond of the quaternary carbon atom C(6) to the carbonyl atom C(5) of 1.568(2) Å is markedly longer than the C(6)–C(19) distance of 1.522(2) Å, which is presumably due to steric interactions between the phenyl rings and the CO function. The exocyclic C(19)–C(20) bond of 1.340(2) Å matches well with the C=C double bonds of **4e**.

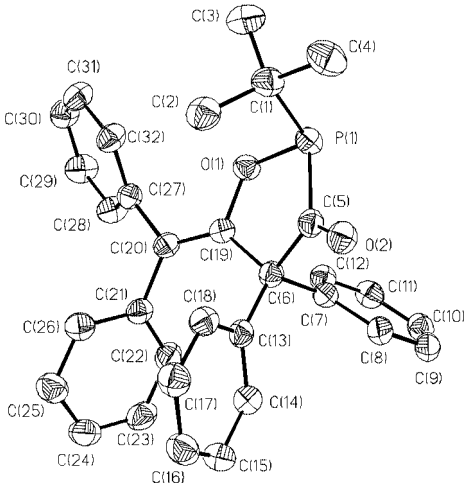


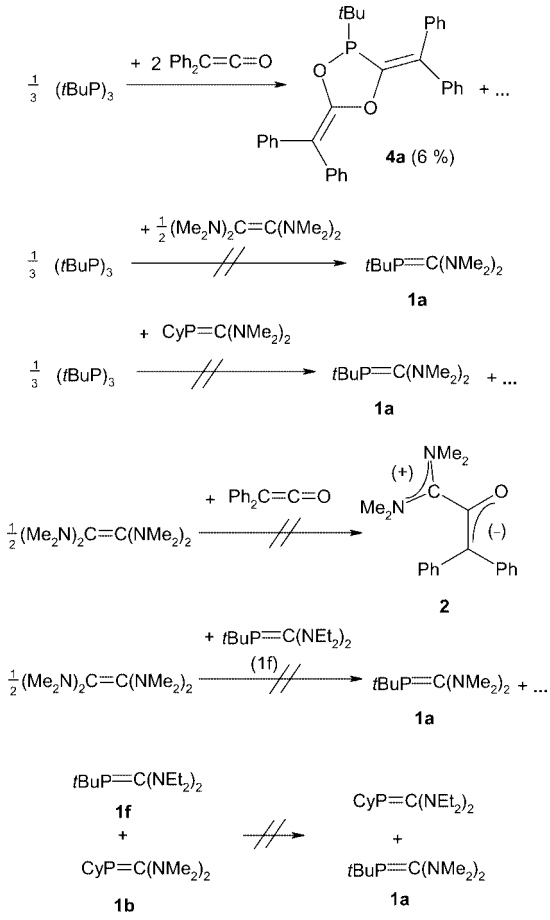
Figure 3. Molecular structure of **6a** in the crystal. Selected bond lengths [Å] and angles [°]: P(1)–C(1) 1.869(2), P(1)–O(1) 1.664(1), O(1)–C(19) 1.406(2), C(6)–C(19) 1.522(2), C(5)–C(6) 1.568(2), P(1)–C(5) 1.861(1), O(2)–C(5) 1.206(2), C(19)–C(20) 1.340(2); O(1)–P(1)–C(1) 103.45(6), C(1)–P(1)–C(5) 100.18(7), O(1)–P(1)–C(5) 90.66(5), P(1)–C(5)–C(6) 107.54(9), C(5)–C(6)–C(19) 103.42(10), O(1)–C(19)–C(6) 110.94(11), P(1)–O(1)–C(19) 117.97(8), P(1)–C(5)–O(2) 127.12(11), O(2)–C(5)–C(6) 125.24(12), O(1)–C(19)–C(20) 118.07(2), C(6)–C(19)–C(20) 130.81(12), C(19)–C(20)–C(21) 123.47(12), C(19)–C(20)–C(27) 121.50(12), C(21)–C(20)–C(27) 114.97(11).

Cross-Coupling and Exchange Experiments

From a formal point of view, the phosphaalkenes employed here display a reactivity similar to tetraaminoalkenes as concerns the homolytic cleavage of the P=C double bond, as the carbene and phosphinidene fragments are efficiently trapped by $Ph_2C{=}C{=}O$. Similar to Wanzlick's observations, however, the question remained open as to whether a genuine equilibrium exists between phosphaalkenes and the electron-sextet species or whether a more complex mechanism is responsible. In order to obtain more information, a number of cross-coupling and exchange experiments were carried out (Scheme 4).

It is known that tri-*tert*-butylcyclotriphosphane serves as a source of the phosphinidene [*t*BuP]. In keeping with this, heating of a mixture of $(t\text{BuP})_3$ and $Ph_2C{=}C{=}O$ in toluene furnished heterocycle **4a** in about 6% yield.

Reaction of $(t\text{BuP})_3$ with $(Me_2N)_2C{=}C(NMe_2)_2$ did not, however, yield the expected phosphaalkene *t*BuP=$C(NMe_2)_2$ (**1a**). Similarly, the treatment of $(t\text{BuP})_3$ with CyP=$C(NMe_2)_2$ (**1b**) to give **1a** failed. Reaction of $(Me_2N)_2C{=}C(NMe_2)_2$ with $Ph_2C{=}C{=}O$ did not afford tractable products as, for example, the adduct **2**. Reaction of $(Me_2N)_2C{=}C(NMe_2)_2$ with *t*BuP=$C(NEt_2)_2$ (**6**) did not give the expected exchange product **1a**. Thus, all these experiments exclude the notable formation of free electron-sextet species. Also, the cross-coupling experiment between *t*BuP=$C(NEt_2)_2$ and CyP=$C(NMe_2)_2$ did not lead to the conceivable metathesis products *t*BuP=$C(NMe_2)_2$ and CyP=$C(NEt_2)_2$.



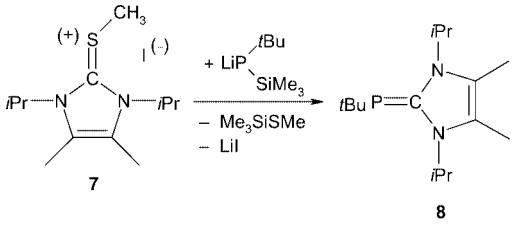
Scheme 4. Attempted exchange experiment.

Synthesis of Labile Phosphaalkenes

According to our results, it is obvious that the phosphaalkenes studied here do show the reactivity of carbenes and phosphinidenes, although transient free electron-sextet species have to be excluded as intermediates. This is in accordance with our knowledge of Wanzlick's equilibrium of tetraaminoalkenes, where spectroscopic evidence of carbenes is restricted to only the most reactive alkenes. Quantum chemical calculations indicate that phosphaalkenes with a cyclic diaminomethylene unit should exhibit a decreased stability towards dissociation,[14] therefore it was obvious to synthesize such a thermolabile phosphaalkene and to study its decomposition.

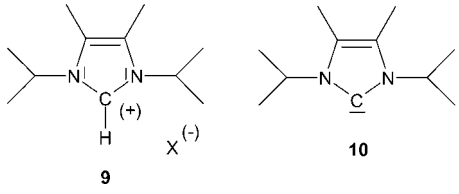
Condensation of [LiP(*t*Bu)($SiMe_3$)] with thiouronium iodide (**7**) in THF led to a red solution, the $^{31}P\{^1H\}$ NMR spectrum of which shows a prominent singlet at $\delta = -5$ ppm

in the region known for inversely polarized phosphaalkenes and which therefore we assigned to compound **8** (Scheme 5).



Scheme 5. Synthesis of **8**.

After distillation, this resonance nearly disappeared, and new intense signals appeared in the NMR spectrum of the distillate. An AB_2 spin system at δ = –108.9 and –70.3 ppm ($J_{A,B}$ = 201 Hz) and a singlet at δ = –57.6 ppm are due to $(t\text{BuP})_3$ and $(t\text{BuP})_4$, respectively, which cover 78% of all the resonances observed. These rings presumably result from the oligomerization of *tert*-butylphosphinidene. The imidazolium cation **9** was identified in the residue of the distillation by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. This ion is most likely formed by protonation of the strong Brønsted base **10**.



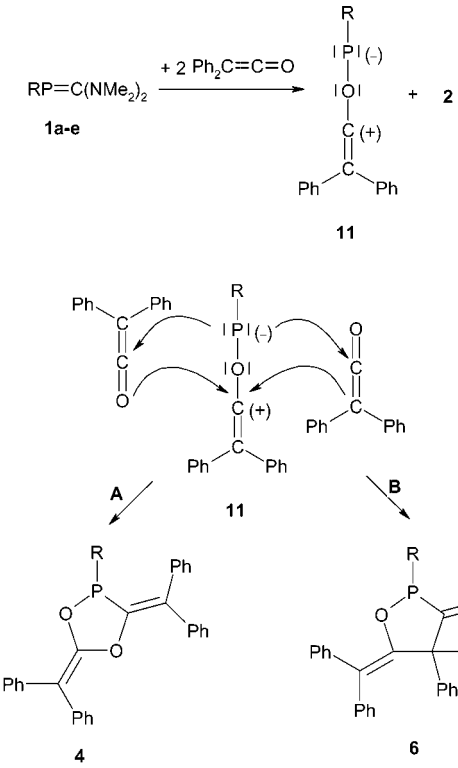
The P=C bonds have been homolytically cleaved and this process is most certainly not part of a genuine equilibrium.

Phosphaalkenes of type **8** have been synthesized previously from equivalent amounts of 1,3,4,5-tetramethylimidazol-2-ylidene and pentaphenylcyclopentaphosphane in 79% yield.[15] Similar results were obtained with 1,3-dimesitylimidazol-2-ylidene and the cyclophosphanes $(PhP)_5$ and $(CF_3P)_4$.[16]

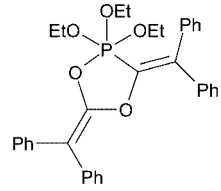
For a mechanism that rationalizes the formation of adduct **2** as well as of the heterocycles **4** and **6a**, we propose the initial cleavage of one molecule of phosphaalkene **1** by reaction with 2 equiv. of $Ph_2C{=}C{=}O$. In addition to **2**, a zwitterion **11** is formed (Scheme 6). Intermediate **11** then undergoes a 1,3-dipolar addition to the C=O bond of another ketene molecule to yield main product **4** (path A). Alternatively, the 1,3-cycloaddition to the C=C double bond of the ketene affords **6a**.

Molecules with the structural feature of a 3,5-dibenzhydrylidene-1,4,2-dioxaphospholane are rare and there are only a few examples documented with pentavalent phosphorus. For example, the reaction of triethyl phosphite with $Ph_2C{=}C{=}O$ furnishes heterocycle **12**.[17]

Similarly, cyclic trialkyl phosphites and 2 equiv. of dimethyl ketene or its dimer give rise to the formation of 2,2,2-trialkoxy-3,5-diisopropylidenephospholanes.[18] Treatment of 3,4-dimethyl-1-phenylphosphole with diphenyl ketene under high pressure (ca. 10 kbar) afforded compound



Scheme 6. Proposed mechanism for the formation of compounds **2**, **4**, and **6**.



13. A cycloreversion of the phosphole to yield a transient phenylphosphinidene has been invoked to rationalize this result.[19]

Conclusions

We have demonstrated that inversely polarized phosphaalkenes $RP{=}C(NMe_2)_2$ (**1a**–**e**) and $t\text{BuP}{=}C(NEt_2)_2$ (**1f**) serve as convenient sources for the generation of phosphinidenes [RP] and carbenes $[(Me_2N)_2C]$ and $[(Et_2N)_2C]$ under mild conditions. These carbenes are trapped by diphenyl ketene, which leads to the formation of the zwitterionic carbene/ketene adducts **2** and **3**. On the other hand, the phosphinidene fragment can also combine with 2 equiv. of ketene in a 1,3-dipolar cycloaddition between the intermediate $RP{-}O{-}C{=}CPh_2$ and $Ph_2C{=}C{=}O$ to give heterocycles **4a**–**e** and **6a**. From cross-coupling and exchange reaction it is obvious that free carbenes and/or phosphinidenes are not involved in these processes.

Experimental Section

General: All reactions were performed under dry, oxygen-free nitrogen using standard Schlenk techniques. The phosphaalkenes *t*BuP=C(NMe$_2$)$_2$ (**1a**),[20] CyP=C(NMe$_2$)$_2$ (**1b**),[21] PhP=C(NMe$_2$)$_2$ (**1d**),[22] MesP=C(NMe$_2$)$_2$ (**1e**),[20] and Me$_3$SiP=C(NMe$_2$)$_2$ (**1i**),[23] as well as Ph$_2$C=C=O,[24] AdPH$_2$,[25] *t*BuP(H)SiMe$_3$,[26] thiouronium salt **7**,[27] and (*t*BuP)$_3$[28] were prepared as described in the literature. Infrared spectra were recorded with a Bruker FT-IR IFS 66 spectrometer. NMR spectra: Bruker AM Avance DRX 500; standards: SiMe$_4$ (^{1}H, ^{13}C), external 85% H$_3$PO$_4$ (^{31}P).

1-AdP(H)SiMe$_3$: A 1.6 M *n*-hexane solution of *n*-butyllithium (59.4 mL, 95.0 mmol) was added dropwise to a solution of 1-AdPH$_2$ (16.8 g, 100.0 mmol) in THF (100 mL) at 0 °C. This slurry was added at 20 °C to a solution of Me$_3$SiCl (11.9 g, 110.0 mmol) in 30 mL of THF, and the mixture was stirred for 16 h. The volatile components were then removed in vacuo and the residue was triturated with *n*-pentane (50 mL). It was then filtered and the filter cake was washed with *n*-pentane (3 × 20 mL). The filtrate was liberated from solvents and the residue was distilled to furnish 15.0 g (69% yield) of 1-AdP(H)SiMe$_3$ as a colorless oil. ^{1}H NMR (CDCl$_3$): δ = 0.25 (d, $^3J_{P,H}$ = 5 Hz, 9 H, SiMe$_3$), 2.16 (d, $^1J_{P,H}$ = 204 Hz, 1 H, PH), 1.6–2.0 (m, 15 H, Ad) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = –85.7 ppm.

1-AdP=C(NMe$_2$)$_2$ (1c): An *n*-hexane solution of *n*-butyllithium (1.6 M, 28.1 mL, 45.0 mmol) was added dropwise, at 0 °C, to a solution of 1-Ad-P(H)SiMe$_3$ (12.2 g, 50 mmol) in THF (50 mL). The resulting slurry was added dropwise to a suspension of pentamethylthiouronium iodide (13.7 g, 50 mmol) in 50 mL of THF. After 16 h of stirring at room temp., the solvent and volatile components were removed in vacuo. The residue was triturated with *n*-pentane (50 mL) and filtered. The filter cake was washed with diethyl ether (3 × 20 mL) and the filtrate was liberated from solvent in vacuo. The residue was distilled in vacuo to give 10.0 g (75%) of **1c** as an orange oil, which slowly solidified to a wax. ^{1}H NMR (C$_6$D$_6$): δ = 1.6–2.0 (m, 15 H, Ad), 2.56 (m, 12 H, NMe$_2$) ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ = 89.7 ppm.

Reaction of 1a–e with Ph$_2$C=C=O (General Procedure): A sample of neat Ph$_2$C=C=O (0.27 g, 1.39 mmol) was transferred dropwise, via a cannula, into a chilled solution (0 °C) of phosphaalkene **1** (0.40 mmol) in 30 mL of *n*-pentane. The resulting slurry was stirred at ambient temp. for 18 h and then filtered. The bright-yellow filter cake was washed with *n*-pentane (3 × 10 mL) and then dried in vacuo. Purification of crude **2** was effected by column chromatography on silica. Impurities were eluted with CH$_2$Cl$_2$ before product **2** was eluted with CH$_3$OH. Removal of solvent in vacuo afforded 0.10 g (85% yield) of bright-yellow, microcrystalline **2**. ^{1}H NMR (CDCl$_3$): δ = 2.74 (s, 6 H, NMe$_2$), 3.21 (s, 6 H, NMe$_2$), 7.00–7.56 (m, 10 H, Ph) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 42.3 [s, N(CH$_3$)$_2$], 42.6 [s, N(CH$_3$)$_2$], 123–130 (s, Ph), 141.6 [s, *C*(NMe$_2$)], 143.0 (s, *C*Ph$_2$), 175.4 (s, CO) ppm. IR (KBr): $\tilde{\nu}$ = 1713 cm^{-1} (CO), 1613 (C=C). MS/ESI: *m*/*z* = 295.0 [**2** + H$^+$]. Peak matching: C$_{19}$H$_{22}$N$_2$O: calcd. 295.18049; found 295.18032. After removal of **2**, the obtained filtrate was treated with powdered NaOH (0.50 g, 12.5 mmol) and stirred at 20 °C for 18 h to destroy the excess of Ph$_2$C=C=O. It was then filtered and the colorless filtrate was concentrated to dryness to afford the heterocycles **4a–e**.

4a (R = *t*Bu): Yield: 0.10 g (53%) of an oily wax. ^{1}H NMR (CDCl$_3$): δ = 0.89 (d, $^3J_{P,H}$ = 12.6 Hz, 9 H, *t*Bu), 7.17–7.37 (m, 20 H, Ph) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 24.7 [d, $^2J_{P,C}$ = 14.9 Hz, C(*C*H$_3$)$_3$], 38.5 [d, $^1J_{P,C}$ = 33.2 Hz, *C*(CH$_3$)$_3$], 93.1 (s, Ph$_2$*C*=CO$_2$), 125.5 (d, $^2J_{P,C}$ = 6.9 Hz, Ph$_2$*C*=COP), 127–131 (20s, Ph), 150.4 (d, $^1J_{P,C}$ = 41.1 Hz, PCO), 157.4 (d, $^2J_{P,C}$ = 11.4 Hz, OCO) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 122.3 ppm (s). IR (KBr): $\tilde{\nu}$ = 1761 cm^{-1} s, 1663 m, 1599 m. MS/EI: *m*/*z* (%) = 476 (27) [**4a**]$^+$, 194 (100) [Ph$_2$C=C=O]$^+$. High resolution MS: calcd. 479.19052; found 479.1902. C$_{32}$H$_{29}$O$_2$P (476.19): calcd. C 80.65, H 6.13; found C 80.40, H 6.12.

4b (R = Cy): Yield: 0.10 g (50%) of a colorless oily wax. ^{1}H NMR (CDCl$_3$): δ = 0.90–1.77 (m, 11 H, Cy), 7.17–7.36 (m, 20 H, Ph) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 26.2 (d, $J_{P,C}$ = 5.7 Hz, Cy), 26.3 (d, $J_{P,C}$ = 6.9 Hz, Cy), 26.7 (d, $J_{P,C}$ = 11.4 Hz, Cy), 27.1 (d, $J_{P,C}$ = 12.6 Hz, Cy), 43.4 (d, $J_{P,C}$ = 34.3 Hz, Cy), 93.7 (s, Ph$_2$*C*=CO$_2$), 125.6 (d, $^2J_{P,C}$ = 28.5 Hz, Ph$_2$*C*=COP), 127–131 (20s, Ph), 137.1 (s, *i*-*C*Ph), 138.4 (s, *i*-*C*Ph), 138.6 (s, *i*-*C*Ph), 138.8 (s, *i*-*C*Ph) 150.3 (d, $^1J_{P,C}$ = 34.3 Hz, PCO), 157.5 (d, $^2J_{P,C}$ = 11.4 Hz, OCO) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 117.8 ppm (s). IR (KBr): $\tilde{\nu}$ = 1727 cm^{-1} s, 1657 m, 1597 m. MS/EI: *m*/*z* (%) = 502 (57) [**4b**]$^+$, 194.1 (100) [Ph$_2$C=C=O]$^+$. High resolution MS: calcd. for C$_{34}$H$_{31}$O$_2$P 502.20617; found 502.20571.

4c (R = Ad): Yield: 0.10 g (45%) of a colorless oily wax. ^{1}H NMR (CDCl$_3$): δ = 1.57–1.91 (m, 15 H, Ad), 7.20–7.38 (m, 20 H, Ph) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 27.8 (d, $J_{P,C}$ = 8.0 Hz, Ad), 36.0 (d, $J_{P,C}$ = 12.6 Hz, Ad), 36.5 (s, Ad), 41.9 (d, $J_{P,C}$ = 33.2 Hz, Ad), 92.5 (s, Ph$_2$*C*=CO$_2$), 125.5 (d, $^2J_{P,C}$ = 9.1 Hz, Ph$_2$*C*=COP), 127–131 (20s, Ph), 137.9 (s, *i*-*C*Ph), 138.5 (s, *i*-*C*Ph), 138.6 (s, *i*-*C*Ph), 139.6 (s, *i*-*C*Ph), 149.5 (d, $^1J_{P,C}$ = 40.0 Hz, P*C*O), 157.7 (d, $^2J_{P,C}$ = 11.4 Hz, O*C*O) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 117.1 ppm (s). IR (KBr): $\tilde{\nu}$ = 1654 cm^{-1} m, 1596 m. MS/EI: *m*/*z* (%) = 554 (53) [**4c**]$^+$, 194 (47) [Ph$_2$C=C=O]$^+$, 165 (58) [CPh$_2$]$^+$, 135 (100) [Ad]$^+$. High resolution MS: calcd. for C$_{38}$H$_{35}$O$_2$P 554.23747; found 554.23790.

4d (R = Ph): Yield 0.10 g (50%) of a colorless oily wax. ^{1}H NMR (CDCl$_3$): δ = 7.02–7.35 (m, 25 H, Ph) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 95.5 (s, Ph$_2$*C*=CO$_2$), 125.9 (d, $^2J_{P,C}$ = 40.0 Hz, Ph$_2$*C*=COP), 127–135 (25s, Ph), 136.8 (d, $J_{P,C}$ = 2.0 Hz, *i*-*C*Ph), 138.1 (s, *i*-*C*Ph), 138.3 (s, *i*-*C*Ph), 138.4 (s, *i*-*C*Ph), 138.6 (s, *i*-*C*Ph), 150.7(d, $^1J_{P,C}$ = 26.3 Hz, PCO), 156.4 (d, $^2J_{P,C}$ = 11.4 Hz, OCO) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 90.6 ppm (s). IR (KBr): $\tilde{\nu}$ = 1764 cm^{-1} s, 1656 m, 1597 m. MS/EI: *m*/*z* (%) = 496 (52) [**4d**]$^+$, 194 (51) [Ph$_2$C=C=O]$^+$. High resolution MS: calcd. for C$_{34}$H$_{25}$O$_2$P 496.15922; found 496.15834.

4e (R = Mes): Yield: 0.10 g (48%) of a colorless oily wax. ^{1}H NMR (CDCl$_3$): δ = 2.28 (s, 3 H, *p*-Me), 3.76 (s, 6 H, *o*-Me), 7.20–7.38 (m, 22 H, Ph + Mes) ppm. ^{13}C{^{1}H} NMR: δ = 52.3 (s, *p*-CH$_3$), 57.0 (s, *o*-CH$_3$), 94.0 (s, Ph$_2$*C*=CO$_2$), 127–131 (26s, Ph + Mes + Ph$_2$*C*=COP), 133.7 (d, $^1J_{P,C}$ = 19.4 Hz, *i*-*C*Mes), 136.8 (s, *i*-*C*Ph), 138.0 (s, *i*-*C*Ph), 138.2 (s, *i*-*C*Ph), 138.7 (s, *i*-*C*Ph), 142.3 (d, $^1J_{P,C}$ < 1 Hz, PCO), 144.8 (d, $^2J_{P,C}$ = 20.6 Hz, OCO) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 103.1 ppm (s). IR (KBr): $\tilde{\nu}$ = 1731 cm^{-1} s, 1649 m, 1601 m. MS/EI: *m*/*z* (%) = 538 (43) [**4e**]$^+$, 194 (51) [Ph$_2$C=C=O]$^+$, 165 (58) [CPh$_2$]$^+$. High resolution MS: calcd. for C$_{37}$H$_{31}$O$_2$P 538.20617; found 538.20634.

3: A sample of diphenyl ketene (0.27 g, 1.39 mmol) was slowly added to a solution of phosphaalkene *t*BuP=C(NEt$_2$)$_2$ (**1f**; 0.10 g, 0.40 mmol) in 30 mL of chilled *n*-pentane (0 °C). The resulting slurry was stirred at room temp. for 18 h and was then filtered. The bright-yellow filter cake was washed with *n*-pentane (3 × 10 mL) and dried in vacuo to give 0.10 g (73%) of **3** as a bright-yellow powder. ^{1}H NMR (CDCl$_3$): δ = 1.0 (br. s, 12 H, CH$_3$), 3.3 (br. s, 8 H, NCH$_2$), 6.96–7.38 (m, 10 H, Ph) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 24.6 (br. s, NCH$_3$), 45.7 (s, NCH$_2$), 126–140 [14 s, Ph + *C*(NEt$_2$)$_2$ + *C*Ph$_2$], 174.4 (s, CO) ppm. MS/EI: *m*/*z* = 351 [**3** +

Table 1. Crystallographic data for **2**, **4e**, and **6**.

	2	**4e**	**6a**
Formula	$C_{19}H_{22}N_2O$	$C_{37}H_{31}O_2P$	$C_{32}H_{29}O_2P$
Color	yellow	colorless	yellow
Size [mm^3]	0.15 × 0.03 × 0.03	0.16 × 0.11 × 0.10	0.30 × 0.30 × 0.18
M_r	294.39	538.59	476.52
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$
a [Å]	8.400(2)	19.4460(2)	16.5600(2)
b [Å]	10.766(1)	6.0100(1)	9.3890(1)
c [Å]	17.539(4)	25.4100(3)	17.2190(3)
β [°]	90	110.2910(6)	109.8970(7)
V [Å^3]	1586.1(5)	2785.39(6)	2517.43(6)
$\rho_{calcd.}$ [g cm^{-3}]	1.233	1.284	1.257
Z	4	4	4
F(000)	632	1136	1008
μ [mm^{-1}]	0.077	0.132	0.137
Θ [°]	3.08 to 20.00	3.13 to 27.48	2.95 to 27.48
T [K]	100	100	150
Refl. measured	2435	55718	31518
Unique refl.	1406	6378	5737
R(int)	0.112	0.046	0.031
No. refl. (I) > 2σ(I)	927	5240	4694
Refined parameters	109	364	319
R_F [$I > 2\sigma(I)$]	0.0733	0.0372	0.0406
wR_F^2 [$I > 2\sigma(I)$]	0.1480	0.0896	0.1037
$\Delta\rho$ max/min [e Å^{-3}]	0.230/–0.213	0.446/–0.314	0.255/–0.356

H^+]. High resolution MS: calcd. for $C_{23}H_{30}N_2O$ 351.24309; found 351.24295.

5: A sample of $Ph_2C{=}C{=}O$ (0.27 g, 1.39 mmol) was combined with an *n*-pentane solution (30 mL) of phosphaalkene Me_3Si-$P{=}C(NMe_2)_2$ (**1i**; 0.05 g, 0.40 mmol) at 0 °C. The resulting solution was stirred at 20 °C for 18 h and then freed from solvent. The residue, consisting of crude **5**, was not purified further. ^{1}H NMR (C_6D_6): δ = 0.11 (s, 9 H, $SiMe_3$), 2.36 (s, 6 H, NMe_2), 2.71 (s, 6 H, NMe_2), 7.00–7.57 (m, 10 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 17.3 ppm (s). MS/EI: *m*/*z* (%) = 398 (47) [**5**]$^+$.

Reaction of $Ph_2C{=}C{=}O$ with (tBuP)$_3$: A mixture of (tBuP)$_3$ (0.10 g, 0.38 mmol) and $Ph_2C{=}C{=}O$ (0.20 g, 1.03 mmol) in 1 mL of toluene was stirred at room temp. for 18 h and then heated to 100 °C for 5 h. The $^{31}P\{^1H\}$ NMR spectrum of the resulting solution showed the resonance of **4a** at δ = 121.9 ppm (ca. 6 mol-% P), a singlet at δ = –57.8 for (tBuP)$_4$ (ca. 14 mol-% P) and the AB pattern of (tBuP)$_3$ at δ = –70.1 and –108.6 ppm.

2-*tert*-Butylphosphanylidene-1,3-diisopropyl-4,5-dimethyl-2,3-dihydro-1*H*-imidazole (8): A 1.6 M *n*-hexane solution of *n*-butyllithium (25 mL, 40.0 mmol) was added dropwise at 0 °C to a solution of tBuP(H)$SiMe_3$ (6.57 g, 40.4 mmol) in THF (35 mL). The mixture was combined with a slurry of 1,3-diisopropyl-4,5-dimethyl-2,3-dihydroimidazol-2-ylidenemethylsulfonium iodide (**7**; 14.5 g, 40.9 mmol) in THF (80 mL) at 0 °C. Stirring was continued at room temp. in the dark for 3 d to give a suspension of a colorless solid and a red solution. A $^{31}P\{^1H\}$ NMR taken from this mixture showed a singlet at δ = 5.0 ppm. The slurry was filtered, and the filtrate was concentrated to dryness. The oily red-brown residue was dissolved in *n*-pentane and filtered. The obtained filter cake was washed with 10 mL of diethyl ether and dried. An ^{1}H NMR spectrum in $CDCl_3$ showed signals at δ = 1.69 [d, $^3J_{H,H}$ = 7.0 Hz, 12 H, $NCH(CH_3)_2$], 2.28 (s, 6 H, CH_3-C=C-CH_3), 4.57 [sept, $^3J_{H,H}$ = 7.0 Hz, 2 H, $NCH(CH_3)_2$], 9.77 ppm (s, 1 H, CH), which agree with the presence of the imidazolium ion **10**. The solvent was then removed from the filtrate and the residual orange oil was distilled. The $^{31}P\{^1H\}$ NMR spectrum of the distillate shows prominent signals at $\delta_{^{31}P}$ = –108.7, –70.5 ppm (AB-spin system) due to (tBuP)$_3$ (ca. 68 mol-% P), –57.6 (tBuP)$_4$ (ca. 10 mol-% P) and 4.3 ppm (**8** ca. 5 mol-% P).

X-ray Crystallography: Details are listed in Table 1. CCDC-273086 (**2**), -273087 (**4e**), and -273088 (**6a**) 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.

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