Phosphaalkenes as Building Blocks in Ene Reactions: Synthesis and Reactivity of 3-Amino-1,2-dihydro-1,2-diphosphetes†

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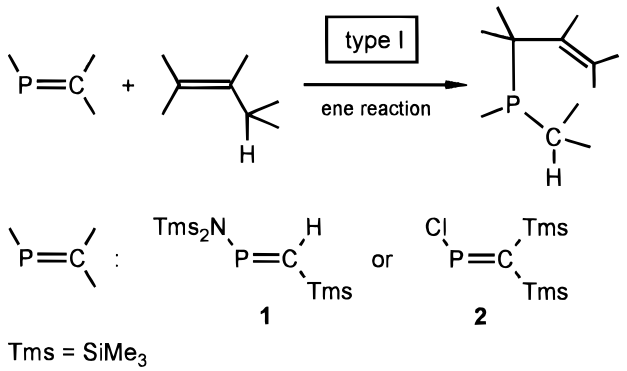
Phospha−ene reactions of the type II between methylidenephosphanes as enophiles and *C*-aminophosphaalkenes possessing allylic hydrogen atoms proceed by P−P bond formation to furnish the corresponding functionalized diphosphanes. Thus, the reaction of the methylidenephosphane **1** with the *C*-amino-substituted ethylidenephosphane **3a** runs smoothly at room temperature to afford the unsymmetrical 1,2-diphosphane **4** as a 60:40 mixture of two diastereomers in 64% yield. Rotation about the P−N bond in **4** is hindered at room temperature, but free enthalpies of activation of $\Delta G^{\ddagger}$(PN) = 16.3 kcal·mol^{-1} (major diastereomer) and 15.2 kcal·mol^{-1} (minor diastereomer) were determined by variable temperature ^{1}H NMR spectroscopy. In contrast, reactions of the ethylidenephosphanes **3a**−**c** with the chlorophosphane **2** as enophile follow an unusual course involving a regiospecific ene reaction of the type II and a subsequent intramolecular ring closure reaction to furnish the 3-amino-1,2-dihydro-1,2-diphosphetes **7a**−**c** in good yields (53−79%). The reactivity of this new class of heterocyclic compounds has been studied exemplarily for product **7a**. The *trans* form of **7a** obtained by synthesis can be converted to the corresponding *cis* form photochemically. Complexation of both phosphorus centers in **7a** is possible by reaction with 2 equiv of diiron nonacarbonyl and gives rise to complex **8**, the constitution of which has been confirmed by X-ray crystallography. Unexpectedly, hydrolysis of **7a** does not proceed by attack at the endocyclic enamine unit but rather by way of P−P bond cleavage to afford the functionalized phosphaalkene **9**. On the other hand, oxidation of **7a** by bis(trimethylsilyl) peroxide takes place with retention of the P_2C_2 skeleton: a selective increase in coordination at P-1 results in the formation of the 1-oxo-1,2-dihydrodiphosphete **10**, the structure of which was confirmed by X-ray crystallography. The reactions of **7a** with the electron-poor acetylenes **11a**−**d** also follow an unusual course. Nucleophilic attack of P-1 at the C≡C triple bond and proton shift lead stereospecifically to the 1-methylene-1,2-dihydro-1,2-diphosphetes **12a**−**d** as thermolabile addition products. The constitution and configuration of **12c** were unambiguously confirmed by X-ray crystallography.

Introduction

The ene reaction, i.e., the "indirect substituting addition" of an unsaturated compound (the enophile) to an alkene possessing allylic hydrogen atoms (the ene), represents one of the most important bond-forming reactions in contemporary organic synthesis.[1] The versatility of this pericyclic reaction is based, above all, on the enormous number and variety of suitable substrates. Low-coordinated compounds of phosphorus may also be employed as reaction partners in addition processes of this type, thus permitting the synthesis of functionalized organophosphorus compounds and, in combination with cycloadditions, the construction of phosphorus−carbon cage compounds.[2] Thus, it was recently shown that the phosphaalkenes **1** and **2** represent excellent enophilic building blocks in ene reactions of the type I (Scheme 1).[3−5] Without exception, all such reactions proceed with the same regiochemistry: the all-carbon ene always undergoes addition with P−C bond formation and transfer of the allylic hydrogen atom of the ene to the carbon

Scheme 1



1 **2**

† Contribution to Organophosphorus Compounds. 120. For part 119, see: Mack, A.; Regitz, M. *Chem. Ber./Recueil* **1997**, *130*, 823−834.

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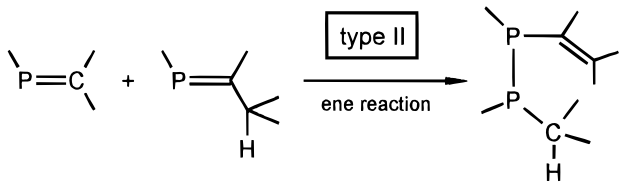
Scheme 2



atom of the P=C double bond, thus making a broad range of β,γ-unsaturated amino- and chlorophosphanes accessible.[6]

In contrast, ene reactions of the type II in which a phosphaalkene takes on the role of the H-donor in place of an all-carbon ene (Scheme 2) are practically unknown. Reactions of this type have previously only been reported for nonkinetically stabilized phosphaalkenes of the Becker type. These compounds dimerize even at room temperature regiospecifically with P−P bond formation to furnish the corresponding diphosphanes with the phosphaalkene playing the part of both the enophile and the ene.[7]

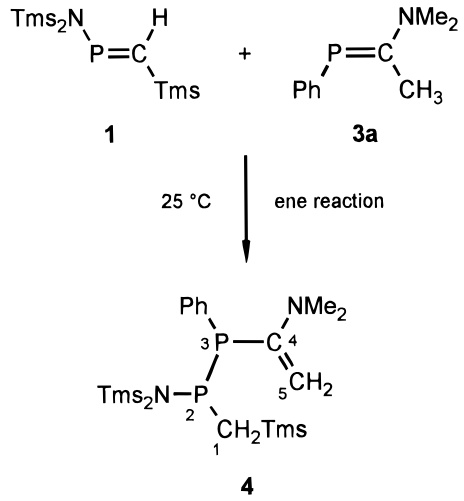
Phospha−ene reactions of the type II with the already proven enophile systems **1** and **2** constitute one of the central aspects of the present paper. For the first time, we have employed as the ene component thermodynamically stabilized *C*-aminophosphaalkenes possessing allylic hydrogen atoms.[8] Addition reactions of this type are expected to open an access to novel, multifunctionalized diphosphanes. Surprisingly, a subsequent cyclization also enabled the construction of previously unknown 3-amino-1,2-dihydro-1,2-diphosphetes; the reactivity of this heterocyclic system constitutes a second major aspect of the present work.

Results and Discussion

Type II Phospha−Ene Reaction of the Ethylidenephosphane 3a with 1 as Enophile. The ene reaction of **1** with an equimolar amount of the *C*-aminosubstituted phosphaalkene **3a** occurs within a few days even at room temperature. After workup by distillation, the addition product **4** is obtained as a yellow oil in 64% yield (Scheme 3). Thus, the first ever ene reaction of the type II between phosphaalkenes with different substitution patterns resulting in the formation of a multifunctionalized diphosphane has been realized.

Since the ene reaction leading to **4** proceeds with the formation of two new asymmetric centers at the two phosphorus atoms, two diastereomeric pairs of enantiomers (ratio 60:40) can be distinguished by spectroscopy. Accordingly, the $^{31}P\{^1H\}$ NMR spectrum exhibits two doublets for each stereoisomer [major diastereomer, δ = 65.0 ppm (P-2), −21.8 ppm (P-3), $^1J_{P,P}$ = 201.4 Hz; minor diastereomer, δ = 57.8 ppm (P-2), −14.0 ppm (P-3), $^1J_{P,P}$ = 203.0 Hz]; these values are in harmony with those previously reported for alkylphenyl-substituted diphosphanes[9] and for 1,2-diaminodiphosphanes.[10] The directly

Scheme 3



adjacent positions of the two phosphorus atoms are unequivocally demonstrated by the magnitude of the $^1J_{P,P}$ coupling constant.[11] Accordingly, the phospha−ene reaction proceeds regiospecifically with P−P bond formation. In the ^1H NMR spectrum of **4**, above all, the proton signals of the 2,3-diphospha-5-pentene skeleton are of high diagnostic value. Two sets of doublet of doublets in the aliphatic region (δ = 0.57−1.67 ppm) are observed for the two diastereotopic methylene protons at C-1 of each diastereomer. In addition to two heteronuclear couplings to the phosphorus atoms for each, further geminal $^2J_{H,H}$ couplings of 14.5 Hz can be detected. This indicates the presence of a CH_2 group and is in harmony with the proposed transfer of an H atom from the ene **3a** to the carbon atom of the heteroalkene **1**. Two doublet of doublets or an apparent triplet at δ = 4.51−5.24 ppm is observed for each of the two, nonequivalent, vinylic protons bonded to C-5; here the splitting results solely from $^1H,^{31}P$ coupling. This, in turn, irrevocably demonstrates the shift of the double bond in the ene with formation of a terminal alkene unit in **4**. The course of the ene addition is further supported by the $^{13}C\{^1H\}$ NMR spectrum of **4**. In particular, the chemical shifts, spin multiplicities (dd each), and the $J_{C,P}$ coupling constants of the aliphatic carbon atom C-1 (δ = 18.4−18.8 ppm) as well as the signals of the two olefinic carbon atoms C-4 and C-5 (δ = 154.3−155.4 and 97.0−98.2 ppm, respectively) of the two diastereomers support the proposed structure (see Supporting Information).

At room temperature, in addition, a more or less pronounced broadening of the two signals for the *N*-bonded trimethylsilyl groups of each diastereomer is observed in both the ^1H NMR and the $^{13}C\{^1H\}$ NMR spectra (see Supporting Information). The latter can be attributed to hindered rotation about the P−N bond; the dynamics of this process have been investigated by variable temperature ^1H NMR spectroscopy (see Supporting Information). At −20 °C rotation about the P−N single bond is already completely frozen, and accordingly, two signals are observed for the nonisochronic, *N*-bonded Tms groups of each of the diastereomers of **4**. When the

(6) Furthermore, the phosphaalkene $PhP{=}CTms_2$ can form ene adducts with all-carbon enes: Suzuki, M.; Sho, K.; Otani, K.; Haruyama, T.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* **1994**, 1191−1192.

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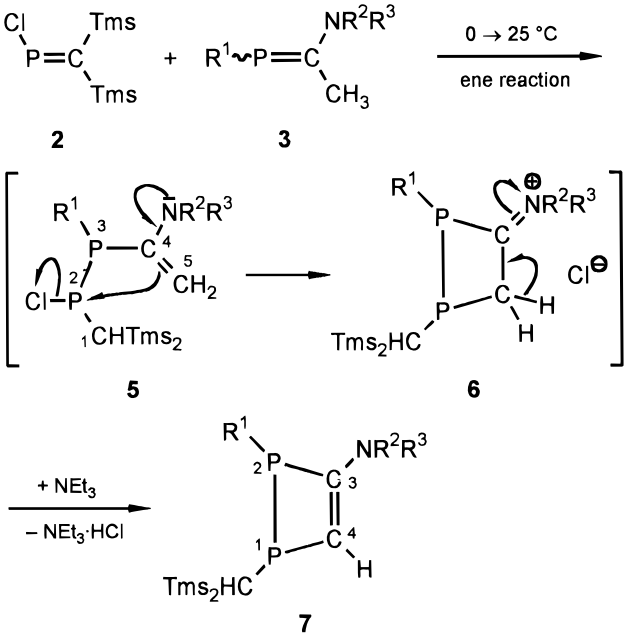
temperature is raised, the two signals for each diastereomer approach each other with increasing signal broadening until they converge to one signal with maximum width (coalescence point). The coalescence temperature for the minor diastereomer is $T_c = 30$ °C, while that for the major diastereomer is appreciably higher ($T_c = 70$ °C). At higher temperature ranges, rotation about the P−N bond should occur so rapidly in comparison to the NMR time scale that differentiation between the two involved trimethylsilyl groups is no longer possible. This has, in principle, also been observed for **4**; however, decomposition of the sample commences at above about 80 °C and effects an extreme broadening of all signals. With the help of the line separations $\Delta\nu$ without exchange (major diastereomer, $\Delta\nu = 138.3$ Hz; minor diastereomer, $\Delta\nu = 28.2$ Hz), free energies of activation of $\Delta G^{\ddagger}$(PN) = 16.3 kcal·mol^{-1} (major diastereomer) and 15.2 kcal·mol^{-1} (minor diastereomer) can be calculated for this rotation process.[12] Hindered rotations about P−N bonds have also been observed for other *N*,*N*-bis(trimethylsilyl)aminophosphanes; however, the activation barrier for **4** is relatively high in comparison to previously reported $\Delta G^{\ddagger}$(PN) values.[13]

Synthesis of New 3-Amino-1,2-dihydro-1,2-diphosphetes via Phospha−Ene Reactions of Type II and Subsequent Cyclization. The reaction of the ethylidenephosphane **3a** with **2** as the enophile follows an unusual course: in the presence of 1 equiv of triethylamine the unsymmetrical 1,2-dihydro-1,2-diphosphete **7a** is obtained selectively as the final product. Separation of the formed ammonium salt and subsequent recrystallization afford **7a** in the form of low-melting, pale yellow needles in very good yield (79%). Even in the absence of the nitrogen base, **7a** can be obtained after distillation, although the yield decreases to less than one-half of that mentioned above (Scheme 4).

The 1:1 composition—with elimination of one molecule of HCl—of the product is clearly demonstrated by elemental analysis and mass spectroscopy (EI-MS, HRMS) with exclusion of the formation of a simple ene adduct. Definitive structural information is provided above all by the $^{31}P\{^1H\}$ NMR spectrum of **7a**, which exhibits an AB spin system at $\delta = -25.9$ (P-1) and −12.4 (P-2) ppm with a remarkably small $^1J_{P,P}$ coupling of 88.0 Hz. The latter is a characteristic feature of this class of heterocyclic compounds.[14,15] In the ^1H NMR spectrum of **7a** the signal of the ring-bonded proton H-4 at $\delta = 4.92$ ppm is of particular diagnostic value. Integration proves conclusively that this signal arises from a single proton. Heteronuclear couplings with the two phosphorus atoms of $^2J_{H,P} = 31.3$ Hz and $^3J_{H,P} = 15.8$ Hz serve as further indications for the presence of a cyclic system. The $^{13}C\{^1H\}$ NMR spectrum of **7a** is also in harmony with the proposed structure. Of particular relevance are, above all, the doublet of doublets signals of the two ring carbon atoms C-3 ($\delta = 154.1$ ppm) and C-4 ($\delta = 98.3$ ppm). The magnitudes of the spin−spin couplings of C-3 ($^1J_{C,P} = 22.5$ Hz and $^2J_{C,P} = 10.5$ Hz) and C-4 ($^1J_{C,P} = 24.1$ Hz and $^2J_{C,P} = 3.2$ Hz) are comparable and thus provide further impressive evidence for the existence of the cyclic P_2C_2 system. A particular feature of the proposed structure is the additional doubling of the C-4 signal ($^1J_{C,H} = 166$ Hz) in the proton-coupled ^{13}C NMR spectrum (see Supporting Information). Since all of the NMR spectra reveal only a single set of signals each, the formation of **7a** must be stereospecific with regard to the positions of the substituents bonded to the phosphorus atoms. Thermodynamic considerations favor a sterically preferred *trans* arrangement. This is supported by the facts that bulb-to-bulb distillation at 180 °C under high vacuum does not result in any isomerization and that X-ray crystallographic analyses of the direct subsequent products all reveal the expected stereochemistry (see the following section).

Scheme 4



3, 5-7	a	b	c
R^1	Ph	Ph	Mes
R^2	Me	Tms	Me
R^3	Me	H	Me

The reactions of **2** with the *C*-amino-substituted phosphaalkenes **3b**,**c** in the presence of 1 equiv of triethylamine follow a completely analogous course. After separation of the formed ammonium chloride and recrystallization (for **7b**) or distillation (for **7c**), the corresponding products are obtained in good yields (53−70%). With the exception of the differences due to the changed substituents R^{1-3}, the NMR data of the derivatives **7b**,**c** do not differ significantly from those of **7a**.

A multistep mechanism must, a priori, be postulated for the formation of products **7** even though ^{31}P NMR monitoring of the reaction mixture does not yield any indications for intermediates (Scheme 4). The first step implies a regiospecific phospha−ene reaction of the type II, hydrogen transfer from **2** to **3**, and P−P bond formation. In contrast to the ene adduct **4**, however, the intermediate **5** contains a relatively good leaving group

(12) The $\Delta G^{\ddagger}$ values were calculated from the equation: $\Delta G^{\ddagger} = 4.57T_c[10.32 + \log(T_c/k_c)]$, with utilization of the expression for determining the rate constant at coalescence, $k_c = \pi\,\Delta\nu/\sqrt{2}$. For a review of dynamic NMR methods, see: Kessler, H. *Angew. Chem.* **1970**, *82*, 237−253; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 155.

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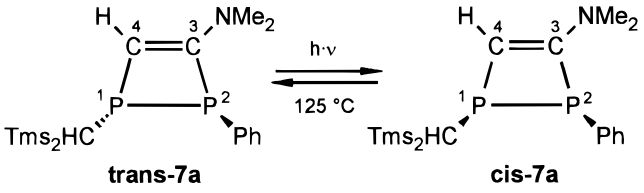
(15) Maigrot, N.; Richard, L.; Charrier, C.; Le Goff, P.; Mathey, F. *Bull. Soc. Chim. Fr.* **1992**, *129*, 76−78.

Scheme 5



at the phosphorus atom P-2. Nucleophilic attack of the enamine carbon atom C-5 at P-2 with extrusion of the chlorine substituent and 1,4-ring closure affords initially the iminium salt **6**. Under the favorable influence of the added nitrogen base, cleavage of HCl from **6** occurs readily with formation of the isolated heterocyclic product **7**. The reaction of **2** with **3** thus provides a novel and general approach to the 1,2-dihydro-1,2-diphosphetes which arouse considerable interest from both synthetic[16] as well as theoretical[17] points of view. A unique structural feature of **7** is the endocyclic enamine unit which may effect significant alterations in the reactivity of this class of heterocyclic compounds.

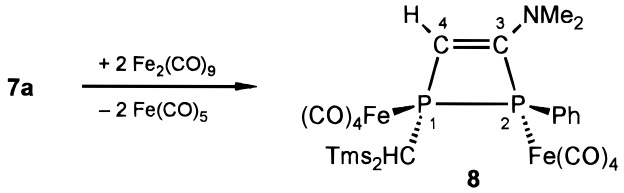
Photochemical and Thermal Isomerization of 7a. When a solution of *trans*-**7a** in CD_2Cl_2 is subjected to photolysis, an equilibrium mixture of the two configurational isomers *trans*-**7a** and *cis*-**7a** (ratio 1:1) is established within 2 days. Thermolysis of this equilibrium mixture in toluene at 125 °C for 18 h results in complete recovery of the starting isomer *trans*-**7a** (Scheme 5). This observation provides further support for the assumption that **7a** arises in the *trans* form in the synthesis shown in Scheme 4.[15]

On the basis of the NMR data for the photolysis mixture, the newly formed product reveals only minor differences in its NMR spectra relative to those for *trans*-**7a**. Observation in support of the formation of *cis*-**7a** is the increase in the $^1J_{P,P}$ coupling constant by more than 16 Hz which may be attributed to a reduction of the dihedral angle between the lone electron pairs at the phosphorus atoms to about 0°.[15,18] Unmistakable indications for the positions of the two *P*-bonded substituents are provided by the ^1H and $^{13}C\{^1H\}$ NMR spectra of *cis*-**7a**. Thus, in comparison to *trans*-**7a**, the signal for the methine proton as well as that of the methine carbon of the $CHTms_2$ substituent experience pronounced shifts to higher field on account of the ring current effect of the aromatic group now in close proximity.

A probable mechanism of the isomerization of *trans*-**7a** to *cis*-**7a** involves the photochemical, disrotatory electrocyclic ring opening of the diphosphacyclobutene *trans*-**7a** with a subsequent thermal, conrotatory electrocyclic ring closure of a putative 1,4-diphosphabutadiene, which cannot be detected by NMR spectroscopy.

Complexation of 7a with Diiron Nonacarbonyl. The reaction of **7a** with 2 equiv of diiron nonacarbonyl in *n*-pentane proceeds selectively to furnish the binuclear complex **8**, which can be obtained as orange-red crystals in 67% yield after column chromatographic purification (Scheme 6).[19]

Scheme 6



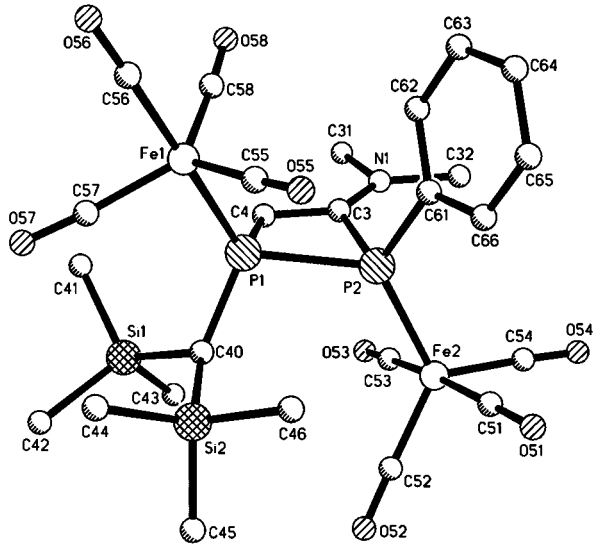


Figure 1. Molecular structure of the 1,2-dihydro-1,2-diphosphete complex **8**.[20]

Elemental analysis and mass spectroscopy (CI-MS) confirm the composition of **8** as being made of one molecule of **7a** and two $Fe(CO)_4$ fragments. The η^1-coordination at the two phosphorus atoms is accompanied by a dramatic deshielding of the ^{31}P NMR signals [δ = 82.3 ppm (P-1), 111.6 ppm (P-2)] and a pronounced reduction of the $^{31}P,^{31}P$ coupling constant to 43.1 Hz.

The *trans* arrangement of the *P*-bound substituents already postulated for compound **7a** is irrevocably confirmed by the X-ray crystal structure analysis of **8** (Figure 1).[20] In the distorted trigonal-bipyramidal coordination polyhedra of the two iron atoms, the phosphorus atom P-1 occupies an axial position in the crystal while the phosphorus atom P-2 is in an equatorial ligand position. The crystal structure analysis also shows that all atoms of the P_2C_2 ring as well as the heavier atoms of the NMe_2 substituent lie in an idealized plane within a maximum deviation of 0.09 Å. The trigonal-planar geometry of the nitrogen atom N-1 as well as the bond lengths in the endocyclic enamine unit [C4−C3, 1.345(7) Å; N1−C3, 1.363(6) Å] are suggestive of the presence of a pπ-system delocalized over the centers (C4−C3−N1). The P1−P2 bond length is rather stretched [2.292(2) Å] and represents the currently longest measured P−P bond separation in all comparable 1,2-dihydro-1,2-diphosphetes investigated to date.[16] The two cyclic P−C single-bond lengths are 1.794(4) (P1−C4) and 1.828(5) (P2−C3) Å and thus differ appreciably; this ring asymmetry is also reflected in the unequal endocyclic bond angles of the ring carbon atoms [103.7(3)° (C4−C3−P2) and 105.5(4)° (C3−C4−P1)].

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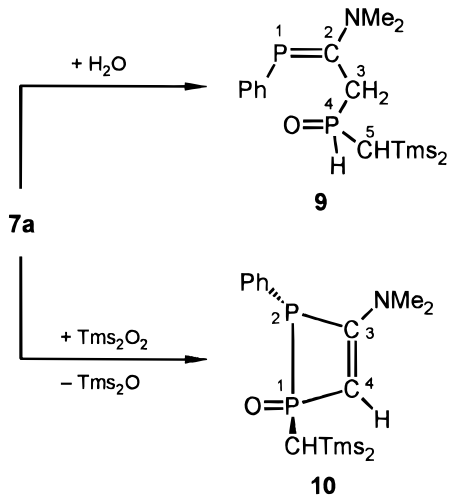
(18) Albrand, J.-P.; Robert, J.-B.; Goldwhite, H. *Tetrahedron Lett.* **1976**, 949−952.

(19) In contrast, the reaction of **7a** with 2 equiv of $W(CO)_5$(thf) leads to the unselective formation of numerous, as yet unidentified, products.

(20) The authors have deposited atomic coordinates, bond lengths, and bond angles for the structure of **8**, **10**, and **12c** with the Cambridge Crystallographic Data Centre. The data can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

Scheme 7



When the reaction is performed with diiron nonacarbonyl in a less than stoichiometric amount, the primarily formed monocomplexed compounds **7a**·Fe(CO)$_4$ [coordination at P-1: $\delta = 9.6$ ppm (P-1), 80.9 ppm (P-2), $^1J_{P,P} = 122.3$ Hz] and **7a**·Fe(CO)$_4$ [coordination at P-2: $\delta = 42.3$ ppm (P-1), 23.9 ppm (P-2), $^1J_{P,P} = 84.3$ Hz] can be detected in addition to the final product **8**. ^{31}P NMR monitoring of the time course of the reaction also reveals that the coordination of the phosphorus atom P-1 proceeds appreciably more rapidly than that of the second phosphorus center P-2. Isolation of the monocoordinated compounds by column chromatography was not successful on account of the practically identical migration properties.

Hydrolysis and Oxidation of 7a. The presence of the unique endocyclic enamine unit in the 1,2-diphosphetes **7** prompted us to investigate the hydrolysis and oxidation behavior of these compounds. In contrast to expectations, hydrolysis of **7a** with 1 equiv of water did not proceed with formation of a cyclic ketone but rather by selective P−P bond cleavage to afford the phosphaalkene **9**, which was obtained in 68% yield after crystallization (Scheme 7).

The incorporation of a water molecule in the product is immediately apparent from the elemental analysis and EI-MS results. Both ^{31}P nuclei experience a significant deshielding in comparison to the starting material. Furthermore, the low-field position of the signal for the $\lambda^3\sigma^2$-phosphorus atom P-1 ($\delta = 93.6$ ppm) is typical for *C*-aminophosphaalkenes,[21,22] whereas the chemical shift of the phosphorus atom P-4 ($\delta = 36.3$ ppm) is in the expected region for a secondary phosphane oxide.[23] In accordance with the structural situation in **9**, a relatively large $^1J_{P,P}$ coupling of 33.2 Hz was observed.[11] Further evidence for the constitution of **9** is provided by the ^{1}H and ^{13}C{^{1}H} NMR spectra. The ^{1}H NMR spectrum and, above all, the signal for the proton bonded to P-4 at $\delta = 7.14$ ppm are characteristic and experience a splitting of $^1J_{H,P} = 461.8$ Hz that is typical for a secondary phosphane oxide.[11] The corresponding splitting is naturally also observed in the proton-coupled ^{31}P NMR signal for P-4.

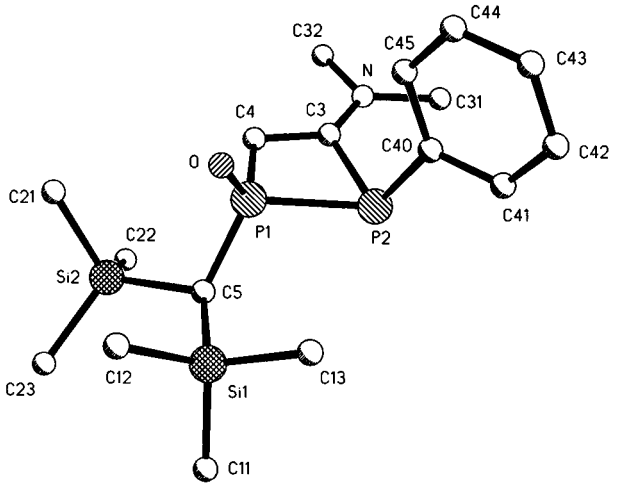


Figure 2. Molecular structure of the 1-oxo-1,2-dihydro-1λ^5,2λ^3-diphosphete **10**.[20]

The presence of a P=C double bond can be deduced securely from the ^{13}C{^{1}H} NMR spectrum by the markedly low-field signal for C-2 ($\delta = 191.4$ ppm) and a direct ^{13}C,^{31}P spin−spin coupling of 66.7 Hz. With regard to the configuration at the P=C double bond, a *trans* orientation of C-3 to the free electron pair of phosphorus atom P-1 must be favored, an assumption supported by the relatively small $^2J_{C,P}$ coupling of 11.4 Hz for this nucleus.[24] Finally, the IR spectrum of **9** should be mentioned since it shows clearly distinguishable bands for P−H stretching ($\nu = 2316$ cm^{-1}) and P=O stretching ($\nu = 1187$ cm^{-1}).

In contrast to hydrolysis, oxidation with 1 equiv of bis(trimethylsilyl) peroxide proceeds with retention of the P_2C_2 skeleton and furnishes the monooxidized 1,2-dihydro-1,2-diphosphete **10** selectively in a yield of 59% (Scheme 7). Use of an excess of bis(trimethylsilyl) peroxide or of hydrogen peroxide or sulfur (in the presence of triethylamine) as oxidizing agent, on the other hand, results in the unselective decomposition of **7a**.

The composition of **10** was confirmed by its EI-MS spectrum (molecular ion peak at $m/z = 383$) and elemental analysis. The increase in coordination of P-1 from $\lambda^3\sigma^3$ to $\lambda^5\sigma^4$ is reflected in a deshielding of both phosphorus nuclei [$\delta = 27.4$ ppm (P-1), 24.2 ppm (P-2)] and a reduction of the $^1J_{P,P}$ coupling constant to 55.8 Hz. Cleavage of the P−P bond can be excluded with certainty. Retention of the heterocyclic system in **10** is also documented by the merely small changes in the ^{1}H and ^{13}C{^{1}H} NMR spectra. One conspicuous fact, however, is the observation of a markedly larger direct ^{13}C,^{31}P coupling of 67.5 Hz for C-4 in comparison to that of the starting material. This can only be interpreted as unequivocal evidence for the oxidation of the immediately adjacent phosphorus atom P-1. The formation of a P=O bond is further substantiated by the appearance of a characteristic band at 1252 cm^{-1} in the IR spectrum of **10**.

X-ray crystallographic analysis of **10** confirmed the increase in coordination at P-1 with complete retention of the rest of the heterocyclic system in that the two *P*-bonded carbon substituents take up the sterically more favorable *trans* geometry (Figure 2).[20] The P1−P2 bond

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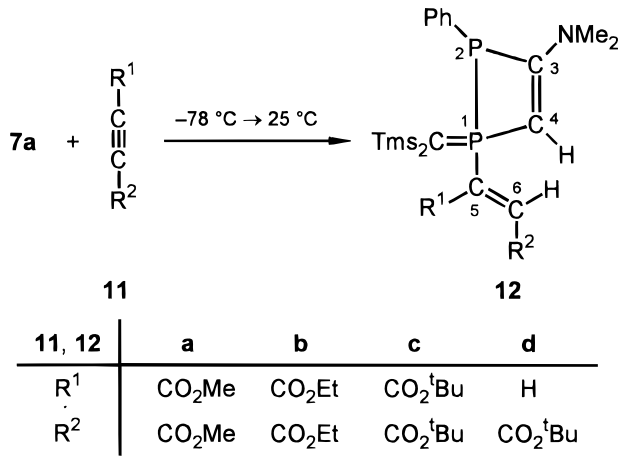
Scheme 8



11, 12	a	b	c	d
R^1	CO_2Me	CO_2Et	$CO_2{}^tBu$	H
R^2	CO_2Me	CO_2Et	$CO_2{}^tBu$	$CO_2{}^tBu$

length of 2.2374(12) Å is in the expected range.[16] This is also the case for the P1−O bond length [1.482(2) Å]. However, the difference in lengths of almost 0.10 Å between the two cyclic P−C bonds is worthy of note [P1−C4, 1.753(3) Å; P2−C3, 1.849(3) Å]; even though comparable values have previously been reported for a 1-thio-1,2-dihydro-1λ^5,2λ^5-diphosphete.[25] The P_2C_2 ring system experiences considerable distortion as reflected in the unequal endocyclic bond angles at the phosphorus and carbon atoms [C4−P1−P2, 78.75(12)°; C3−P2−P1, 72.91(12)°; C3−C4−P1, 102.8(3); C4−C3−P2, 104.6(3)°]. In addition, a slight twisting of the heterocyclic system is observed [torsion angle C4−P1−P2−C3 of 5.6°].

Reaction of 7a with Electron-Deficient Acetylenes. It is well known that enamines react with electron-deficient acetylenes via [2 + 2] cycloaddition to give cyclobutenes.[26] Thus, application of this principle to the 3-amino-1,2-dihydro-1,2-diphosphetes **7** described here would be expected to provide an access to six-membered heterocyclic systems.

The reaction of **7a** with the electron-deficient alkynes **11a**−**d** occurs at low temperature (−78 °C for **11a**−**c** or −30 °C for **11d**) and is accompanied by a change in color of the reaction mixture from yellow to deep red. After filtration through Celite, the products **12a**−**d** can be isolated in very good yields (74−82%) as deep red, viscous oils (**12a**,**b**,**d**) or in the form of deep red crystals (**12c**) (Scheme 8). However, these products are not the initially expected [2 + 2] cycloadducts of **7a** with **11a**−**d** but rather the 1-methylene-1,2-dihydro-1,2-diphosphetes **12a**−**d**, formed stereospecifically by nucleophilic attack of the phosphorus atom P-1 in **7a** on the electron-deficient acetylene **11** with subsequent transfer of the acidic proton of the $CHTms_2$ substituent to the anionic center C-6. As already noticed in the complexation and oxidation of **7a**, in this case also the phosphorus atom P-1 proves to be the most reactive center in the molecule. The new heterocyclic products **12a**−**d** are thermolabile compounds: when they are subject to the conditions of bulb-to-bulb distillation, decomposition with reformation of **7a** occurs.

The compositions and constitutions of the addition products **12a**−**d** were deduced from their EI-MS spectra (molecular ion peak), elemental analyses (**12a**−**c**), and

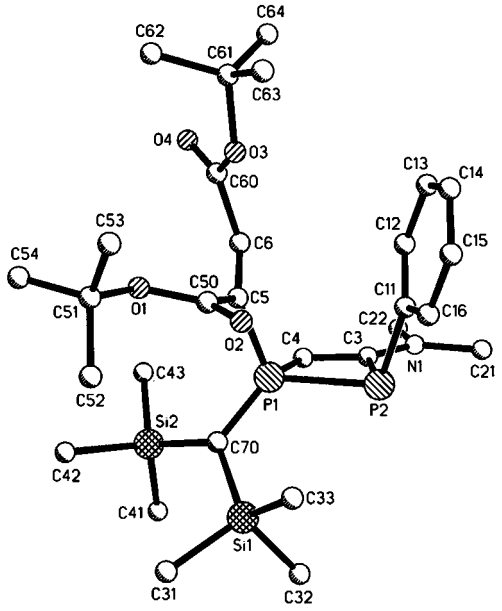


Figure 3. Molecular structure of the 1-methylene-1,2-dihydro-1,2-diphosphete **12c**.[20]

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR experiments. Thus, the phosphorus signal of P-1 experiences a pronounced low-field shift (δ = 23.0 to 25.2 ppm compared to δ = −25.9 ppm in **7a**) on account of the coordination increase from $\lambda^3\sigma^3$ to $\lambda^5\sigma^4$, while that for P-2, as expected, is only slightly deshielded (δ = −7.5 to −3.9 ppm compared to δ = −12.4 ppm in **7a**). The $^{31}P,^{31}P$ coupling increases concomitantly to 104.2−121.8 Hz. The ^1H NMR spectra of **12a**−**d** convincingly confirm the retention of the endocyclic enamine unit as well as the proton transfer from the $CHTms_2$ substituent to the electron-deficient acetylene. This proton, now bonded to C-6, gives rise to a characteristic doublet (**12a**−**c**) or doublet of doublets (**12d**) at δ = 5.89−6.66 ppm. Because of the relatively small vicinal $^3J_{H,P}$ coupling of this proton of only 18.1−19.5 Hz, a *cis* orientation between P and H can be deduced.[11] This assumption is further supported by an additional, homonuclear $^3J_{H,H}$ coupling of 16.2 Hz for this proton in the case of **12d**, which again implicates a *trans* arrangement of H-6 and H-5. Retention of the original heterocyclic ring in the product is once more apparent from the minimal changes in the $^{13}C\{^1H\}$ NMR data of the P_2C_2 system. The presence of an exocyclic methylenephosphorane unit is unequivocally confirmed by the strong shielding of the methylene carbon atom of the $CTms_2$ group (δ = 10.8−14.3 ppm). Moreover, the signals of the olefinic carbon atoms of the alkenyl substituent at δ = 141.9−146.8 (C-5) and δ = 133.3−135.3 (C-6) ppm, which both exhibit the appropriate $^{13}C,^{31}P$ couplings (see Supporting Information), are characteristic for such a structure.

The constitution and configuration of the addition product **12c** were confirmed by X-ray crystallography (Figure 3).[20] The geometry of the C=C double bond of the vinyl substituent in **12c** demonstrates that it is a derivative of maleic acid; furthermore, a *trans* arrangement of the phenyl and $CTms_2$ substituents bonded to phosphorus is observed, thus providing further support for the assumed stereochemistry of **7a**. Even though the ring atoms as well as the heavier atoms of the NMe_2 substituent lie in an idealized plane within a maximum deviation of 0.02 Å, the central P_2C_2 unit experiences

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considerable distortion (also in comparison to **8**). This is reflected in the clearly differing P−C single [P1−C4, 1.769(5) Å; P2−C3, 1.839(5) Å] and the endocyclic bond angles at the phosphorus and carbon atoms [C4−P1−P2, 78.6(2)°; C3−P2−P1, 73.4(2)°; C3−C4−P1, 102.4(4); C4−C3−P2, 105.3(4)°]. In contrast, the P1−P2 bond length of 2.240(2) Å is inconspicuous for 1,2-dihydro-1,2-diphosphetes.[16] The presence of an exocyclic, nonstabilized phosphorus ylid element is documented by a typically short P1−C70 separation of 1.682(5) Å and an almost planar arrangement of the substituents about the carbon C70 (Σ 358.3°).[27]

Conclusions

Phospha−ene reactions of the type II can not only be exploited for the construction of multifunctionalized 1,2-diphosphanes but also, in combination with a cyclization process, provide a new and efficient access to previously unknown 3-amino-1,2-dihydro-1,2-diphosphetes. The ene additions always proceed with uniform regiochemistry through P−P bond formation and transfer of the ene to the carbon atom of the methylidenephosphane.

Experimental Section

General. All reactions were performed under argon (purity > 99.998%) in previously evacuated and baked-out reactions vessels. The solvents were dried according to standard procedures (toluene, Na; ether, Na/K alloy; *n*-pentane, $LiAlH_4$) and then distilled and stored under argon prior to use. Compounds **1**,[28] **2**,[29] **3a**,[21] **3b**,[22] and bis(trimethylsilyl) peroxide[30] were prepared by published methods. Compound **3c** was prepared by the reaction of mesitylphosphane[31] with *N*,*N*-dimethylacetamide dimethyl acetal (Aldrich) and purified by distillation (see Supporting Information). Compounds **11a**−**d** were purchased from Aldrich and used without further purification. Column chromatography was performed in water-cooled glass tubes with a positive pressure of argon on the column. Alumina was heated for 12 h in vacuo and then deactivated with 4% water (Brockmann activity II). Melting points are uncorrected (heating rate: 2 °C/min). All NMR spectra were taken on Bruker AC 200 and AMX 400 spectrometers.

4-(Dimethylamino)-2-[bis(trimethylsilyl)amino]-1-(trimethylsilyl)-3-phenyl-2,3-diphospha-4-pentene (4). A solution of **1** (0.61 g, 2.2 mmol) and **3a** (0.39 g, 2.2 mmol) in 4 mL of toluene was stirred at rt for 72 h. The solvent was evaporated under vacuum, and the remaining residue was subjected to bulb-to-bulb distillation, which afforded an inseparable 60:40 mixture of the diastereomers of **4** as a yellow oil (0.64 g, 64%): bp 160 °C/5 × 10^{-3} mbar; $^{31}P\{^1H\}$ NMR ($CDCl_3$) major isomer δ −21.8 (d, $J_{P,P}$ = 201.4 Hz), 65.0 (d, $J_{P,P}$ = 201.4 Hz), minor isomer δ −14.0 (d, $J_{P,P}$ = 203.0 Hz), 57.8 (d, $J_{P,P}$ = 203.0 Hz); ^1H NMR (toluene-d_8) major isomer δ 0.12 (d, br, 9H), 0.21 (d, $J_{H,P}$ = 0.7 Hz, 9H), 0.45 (s, br, 9H), 1.27 (ddd, $J_{H,P}$ = 4.1, 2.6 Hz, $J_{H,H}$ = 14.5 Hz, 1H), 1.67 (ddd, $J_{H,P}$ = 4.3, 3.0 Hz, $J_{H,H}$ = 14.5 Hz, 1H), 2.55 (s, 6H), 4.51 (dd, $J_{H,P}$ = 11.4, 2.5 Hz, 1H), 4.69 (app t, $J_{H,P}$ = 3.6, 3.6 Hz, 1H), 6.98−7.16 (m, 3H), 7.83−7.87 (m, 2H), minor diastereomer δ −0.06 (d, $J_{H,P}$ = 0.7 Hz, 9H), 0.51 (s, br, 18H), 0.57 (ddd, $J_{H,P}$ = 4.5, 4.0 Hz, $J_{H,H}$ = 14.5 Hz, 1H), 1.36 (ddd, $J_{H,P}$ = 4.4, 3.6 Hz, $J_{H,H}$ = 14.5 Hz, 1H), 2.54 (s, 6H), 4.69 (dd, $J_{H,P}$ = 7.3, 4.0 Hz, 1H), 5.24 (dd, $J_{H,P}$ = 4.7, 2.1 Hz, 1H), 6.98−7.16 (m, 3H), 7.67−7.71 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) major diastereomer δ 0.9 (d, $J_{C,P}$ = 4.8 Hz), 4.8 (d, $J_{C,P}$ = 14.5 Hz), 7.1 (d, $J_{C,P}$ = 8.8 Hz), 18.8 (dd, $J_{C,P}$ = 51.0, 14.1 Hz), 42.1 (d, $J_{C,P}$ = 10.4 Hz), 98.2 (dd, $J_{C,P}$ = 21.7, 7.2 Hz), 128.6 (d, $J_{C,P}$ = 6.4 Hz), 129.0 (s), 135.0 (dd, $J_{C,P}$ = 18.1, 6.0 Hz), 137.9 (dd, $J_{C,P}$ = 21.7, 13.7 Hz), 155.4 (dd, $J_{C,P}$ = 16.5, 10.0 Hz), minor diastereomer δ 0.5 (d, $J_{C,P}$ = 5.6 Hz), 5.3 (d, br), 6.9 (d, br), 18.4 (dd, $J_{C,P}$ = 51.4, 15.3 Hz), 42.0 (d, $J_{C,P}$ = 8.8 Hz), 97.0 (dd, $J_{C,P}$ = 25.3, 3.6 Hz), 128.8 (d, $J_{C,P}$ = 8.0 Hz), 129.3 (s), 135.3 (dd, $J_{C,P}$ = 19.7, 4.4 Hz), 136.7 (dd, $J_{C,P}$ = 21.7, 11.2 Hz), 154.3 (dd, $J_{C,P}$ = 14.1, 14.1 Hz); IR (film) 1646 (C═C) cm^{-1}; MS (EI, 70 eV) *m*/*z* (rel int) 456 (6, M^+). Anal. Calcd for $C_{20}H_{42}N_2P_2Si_3$: C, 52.59; H, 9.27; N, 6.13. Found: C, 52.4; H, 9.1; N 6.1. HRMS calcd 456.2132, found 456.2136.

General Procedure for the Preparation of the 3-Amino-1,2-dihydro-1,2-diphosphetes 7a-c. To a stirred solution of **3a**, **3b**, or **3c** (2.0 mmol) and triethylamine (0.20 g, 2.0 mmol) in 4 mL of toluene was added dropwise at 0 °C a solution of **2** (0.45 g, 2.0 mmol) in 4 mL of toluene. Subsequently the reaction mixture was allowed to warm to rt and stirred for 12 h. After removal of the solvent under vacuum, the residue was taken up in 5 mL of *n*-pentane and filtered through a glass D3 sinter filled to a depth of 3 cm with Celite. After two washings with *n*-pentane (5 mL each), the combined filtrates were evaporated to dryness. The resultant yellow solid was recrystallized from *n*-pentane at −20 °C to yield pure **7a** or **7b**, while **7c** was purified by bulb-to-bulb distillation.

***trans*-1-[Bis(trimethylsilyl)methyl]-3-(dimethylamino)-2-phenyl-1,2-dihydro-1,2-diphosphete (*trans*-7a):** pale yellow crystals (0.58 g, 79%); mp 70 °C; bp 180 °C/5 × 10^{-3} mbar; $^{31}P\{^1H\}$ NMR (C_6D_6) δ −25.9 (d, $J_{P,P}$ = 88.0 Hz), −12.4 (d, $J_{P,P}$ = 88.0 Hz); ^1H NMR ($CDCl_3$) δ 0.11 (s, 9H), 0.14 (s, 9H), 0.82 (dd, $J_{H,P}$ = 11.5, 2.5 Hz, 1H), 2.60 (s, 6H), 4.92 (dd, $J_{H,P}$ = 31.3, 15.8 Hz, 1H), 7.27−7.29 (m, 3H), 7.49−7.53 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 1.8 (app t, $J_{C,P}$ = 4.4, 4.4 Hz), 2.3 (d, $J_{C,P}$ = 4.8 Hz), 19.5 (d, $J_{C,P}$ = 68.3 Hz), 38.9 (d, $J_{C,P}$ = 4.0 Hz), 98.3 (dd, $J_{C,P}$ = 22.5, 10.5 Hz), 129.0 (d, $J_{C,P}$ = 6.4 Hz), 129.9 (s), 133.5 (dd, $J_{C,P}$ = 18.5, 4.8 Hz), 136.1 (d, $J_{C,P}$ = 34.5 Hz), 151.1 (dd, $J_{C,P}$ = 24.1, 3.2 Hz); IR (KBr) 1636 (C═C) cm^{-1}; MS (EI, 70 eV) *m*/*z* (rel int) 367 (100, M^+). Anal. Calcd for $C_{17}H_{31}NP_2Si_2$: C, 55.55; H, 8.50; N, 3.81. Found: C, 55.6; H, 8.4; N, 3.7. HRMS calcd 367.1471, found 367.1469.

1-[Bis(trimethylsilyl)methyl]-2-phenyl-3-[(trimethylsilyl)amino]-1,2-dihydro-1,2-diphosphete (7b): yellow powder (0.58 g, 70%); mp 94 °C; $^{31}P\{^1H\}$ NMR (C_6D_6) δ −19.7 (d, $J_{P,P}$ = 87.5 Hz), −2.1 (d, $J_{P,P}$ = 87.5 Hz); ^1H NMR (C_6D_6) δ 0.24 (s, 9H), 0.32 (s, 18H), 1.08 (dd, $J_{H,P}$ = 12.2, 4.6 Hz, 1H), 5.63 (dd, $J_{H,P}$ = 40.3, 25.5 Hz, 1H), 5.94 (s, br, 1H), 7.07−7.19 (m, 5H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ −0.3 (s), 1.3 (s), 1.8 (s), 18.0 (d, $J_{C,P}$ = 68.2 Hz), 105.7 (dd, $J_{C,P}$ = 23.3, 12.5 Hz), 128.7 (d, $J_{C,P}$ = 7.2 Hz), 129.8 (s), 134.0 (dd, $J_{C,P}$ = 18.5, 5.0 Hz), 135.9 (d, $J_{C,P}$ = 35.9 Hz), 148.7 (dd, $J_{C,P}$ = 23.7, 5.8 Hz); IR (*n*-pentane) 3215 (NH), 1619 (C═C) cm^{-1}; MS (EI, 70 eV) *m*/*z* (rel int) 411 (19, M^+).

1-[Bis(trimethylsilyl)methyl]-3-(dimethylamino)-2-mesityl-1,2-dihydro-1,2-diphosphete (7c): greenish-yellow powder (0.43 g, 53%); mp 103 °C; bp 190 °C/5 × 10^{-3} mbar; $^{31}P\{^1H\}$ NMR (C_6D_6) δ −41.0 (d, $J_{P,P}$ = 110.7 Hz), −23.8 (d, $J_{P,P}$ = 110.7 Hz); ^1H NMR (C_6D_6) δ 0.32 (s, 9H), 0.36 (s, 9H), 1.08 (dd, $J_{H,P}$ = 11.8, 4.1 Hz, 1H), 2.12 (s, 3H), 2.44 (s, 6H), 2.82 (s, 6H), 4.91 (dd, $J_{H,P}$ = 31.4, 19.0 Hz, 1H), 6.77 (s, 2H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 1.4 (dd, $J_{C,P}$ = 5.7, 3.4 Hz), 2.0 (d, $J_{C,P}$ = 4.6 Hz), 17.6 (d, $J_{C,P}$ = 68.7 Hz), 21.1 (s), 22.7 (s), 38.4 (d, $J_{C,P}$ = 3.8 Hz), 94.4 (dd, $J_{C,P}$ = 31.3, 9.9 Hz), 128.8 (d, $J_{C,P}$ = 13.7 Hz), 130.0 (d, $J_{C,P}$ = 3.0 Hz), 139.9 (s), 146.3 (m), 153.6 (dd, $J_{C,P}$ = 25.2, 7.6 Hz); IR (KBr) 1601 (C═C) cm^{-1}; MS (EI, 70 eV) *m*/*z* (rel int) 409 (7, M^+). Anal. Calcd for $C_{20}H_{37}NP_2Si_2$: C, 58.64; H, 9.10; N, 3.42. Found: C, 58.39; H, 9.15; N, 3.42.

Photochemical and Thermal Isomerization of 7a. An NMR tube containing a solution of *trans*-**7a** in CD_2Cl_2 was placed in a photolysis apparatus and irradiated under cooling with water for 2 days with a medium-pressure mercury lamp, which resulted in the formation of *cis*-**7a** in a 1:1 ratio with *trans*-**7a**. From this mixture, the following data for *cis*-**7a** were

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obtained: $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −26.9 (d, $J_{P,P}$ = 104.6 Hz), 6.4 (d, $J_{P,P}$ = 104.6 Hz); ^1H NMR (CD_2Cl_2) δ −0.10 (s, 9H), −0.06 (dd, $J_{H,P}$ = 12.4, 4.9 Hz, 1H), 0.20 (s, 9H), 2.74 (s, 6H), 5.04 (dd, $J_{H,P}$ = 30.8, 10.3 Hz, 1H), 7.42−7.48 (m, 3H), 7.53−7.57 (m, 2H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 2.2 (d, $J_{C,P}$ = 7.2 Hz), 3.0 (dd, $J_{C,P}$ = 5.6, 4.0 Hz), 13.5 (d, $J_{C,P}$ = 80.3 Hz), 39.9 (d, $J_{C,P}$ = 6.4 Hz), 103.6 (dd, $J_{C,P}$ = 17.7, 14.5 Hz), 130.0 (d, $J_{C,P}$ = 7.2 Hz), 131.2 (s), 136.0 (d, $J_{C,P}$ = 18.5 Hz), 137.7 (dd, $J_{C,P}$ = 41.4, 2.0 Hz), 153.4 (d, $J_{C,P}$ = 21.7 Hz).

***trans*-1:2-η:η-[1-[Bis(trimethylsilyl)methyl]-3-(dimethylamino)-2-phenyl-1,2-dihydro-1,2-diphosphete]bis[tetracarbonyliron(0)] (8).** A suspension of **7a** (0.37 g, 1.0 mmol) and diiron nonacarbonyl (0.74 g, 2.0 mmol) in 10 mL of *n*-pentane was stirred at rt for 24 h. After evaporation of the mixture under vacuum, the resultant deep red residue was purified by column chromatography on alumina. Elution with *n*-pentane provided crude **8**. Recrystallization from *n*-pentane at −20 °C gave pure **8** as orange-red crystal cubes (0.47 g, 67%): mp 140 °C; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 82.3 (d, $J_{P,P}$ = 43.1 Hz), 111.6 (d, $J_{P,P}$ = 43.1 Hz); ^1H NMR (C_6D_6) δ 0.37 (s, 9H), 0.46 (s, 9H), 2.08 (dd, $J_{H,P}$ = 19.2, 14.6 Hz, 1H), 2.21 (s, 6H), 5.00 (dd, $J_{H,P}$ = 54.1, 24.3 Hz, 1H), 7.06−7.21 (m, 3H), 7.76−7.80 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 3.6 (s), 4.2 (s), 25.1 (d, $J_{C,P}$ = 28.0 Hz), 40.2 (s), 104.6 (dd, $J_{C,P}$ = 44.9, 22.0 Hz), 129.5 (d, $J_{C,P}$ = 9.3 Hz), 132.5 (s), 132.7 (d, $J_{C,P}$ = 17.0 Hz), 133.5 (d, $J_{C,P}$ = 10.2 Hz), 148.5 (dd, $J_{C,P}$ = 41.5, 26.3 Hz), 215.0 (d, $J_{C,P}$ = 15.3 Hz), 215.7 (d, $J_{C,P}$ = 10.2 Hz); IR (KBr) 2062 (CO), 2040 (CO), 1992 (CO), 1978 (CO), 1962 (CO), 1950 (CO), 1936 (CO), 1926 (CO) cm^{-1}; MS (CI, isobutane, 120 eV) *m*/*z* (rel int) 704 (8, $M^+ + H$). Anal. Calcd for $C_{25}H_{31}Fe_2NO_8P_2Si_2$: C, 42.69; H, 4.44; N, 1.99. Found: C, 42.8; H, 4.5; N, 1.9.

Crystal Data and Summary of Data Collection Parameters for 8: [20] diffractometer Siemens P4; radiation Mo Kα; M = 703.33 g/mol; monoclinic $P2_1/c$; a = 17.317(3) Å, b = 9.566(2) Å, c = 20.215(4) Å; β = 96.17(3)°; V = 3329.3(11) Å^3; Z = 4; d_{calcd} = 1.403 g/cm^3; Θ range 2.03−24.00°; structure solution by direct methods (SHELXS-86[32]), structure refinement by full-matrix least-squares (SHELXL-93[33]) against F^2; number of reflections collected 6577, number of observed reflections 5221; R = 0.0491, w_R = 0.1002.

(*E*)-2-(Dimethylamino)-4-oxo-1-phenyl-5-bis(trimethylsilyl)-1λ^3,4λ^5-diphospha-1-pentene (9). A solution of **7a** (0.31 g, 0.8 mmol) in 5 mL of ether was treated with an equimolar amount of water and stirred for 6 h at rt. The reaction mixture was concentrated in vacuo. After the concentrated solution cooled to 3 °C, pure **9** precipitated as pale yellow needles (0.22 g, 68%): mp 101 °C; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 36.3 (d, $J_{P,P}$ = 33.2 Hz), 93.6 (d, $J_{P,P}$ = 33.2 Hz); ^1H NMR (C_6D_6) δ 0.13 (s, 9H), 0.17 (s, 9H), 0.25 (m, 1H), 2.88 (d, $J_{H,P}$ = 4.6 Hz, 6H), 3.01−3.11 (m, 1H), 3.61−3.69 (m, 1H), 7.01−7.06 (m, 1H), 7.09−7.13 (m, 2H), 7.14 (dm, $J_{H,P}$ = 461.8 Hz, 1H), 7.54−7.58 (m, 2H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 0.8 (d, $J_{C,P}$ = 3.8 Hz), 2.1 (d, $J_{C,P}$ = 2.9 Hz), 18.8 (d, $J_{C,P}$ = 37.2 Hz), 40.0 (dd, $J_{C,P}$ = 52.5, 11.4 Hz), 43.0 (d, $J_{C,P}$ = 18.1 Hz), 127.4 (s), 128.9 (d, $J_{C,P}$ = 2.9 Hz), 136.6 (d, $J_{C,P}$ = 11.4 Hz), 143.5 (d, $J_{C,P}$ = 46.7 Hz), 191.4 (dd, $J_{C,P}$ = 66.7, 8.6 Hz); IR (KBr) 2316 (PH), 1187 (P=O) cm^{-1}; MS (EI, 70 eV) *m*/*z* (rel int) 385 (24, M^+). Anal. Calcd for $C_{17}H_{33}NOP_2Si_2$: C, 52.96; H, 8.63; N, 3.63. Found: C, 52.68; H, 8.56; N, 3.52.

***trans*-5-[Bis(trimethylsilyl)methyl]-3-(dimethylamino)-1-oxo-2-phenyl-1λ^5,2λ^3-dihydro-1,2-diphosphete (10).** To a stirred solution of **7a** (0.26 g, 0.7 mmol) in 4 mL of toluene was added dropwise at rt a solution of bis(trimethylsilyl) peroxide (0.13 g, 0.7 mmol) in 3 mL of toluene. After the mixture stirred for 4 h, the solvent was removed under vacuum. The resultant solid was recrystallized from toluene at 3 °C to furnish **10** as colorless crystals (0.16 g, 59%): mp 137 °C; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 24.2 (d, $J_{P,P}$ = 55.8 Hz), 27.4 (d, $J_{P,P}$ = 55.8 Hz); ^1H NMR (C_6D_6) δ 0.27 (s, 9H), 0.29 (s, 9H), 0.86 (dd, $J_{H,P}$ = 12.2, 2.2 Hz, 1H), 2.15 (s, 6H), 5.11 (app t, $J_{H,P}$ = 13.2, 13.2 Hz, 1H), 7.08−7.20 (m, 3H), 7.85−7.89 (m, 2H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 1.3 (d, $J_{C,P}$ = 1.6 Hz), 1.8 (s), 25.8 (dd, $J_{C,P}$ = 26.2, 14.9 Hz), 40.1 (s), 106.0 (dd, $J_{C,P}$ = 67.5, 36.9 Hz), 128.2 (d, $J_{C,P}$ = 4.8 Hz), 129.6 (s), 131.1 (dd, $J_{C,P}$ = 24.9, 12.9 Hz), 133.5 (dd, $J_{C,P}$ = 15.7, 7.6 Hz), 159.8 (dd, $J_{C,P}$ = 16.1, 4.0 Hz); IR (KBr) 1635 (C=C), 1252 (P=O) cm^{-1}; MS (EI, 70 eV) *m*/*z* (rel int) 383 (25, M^+). Anal. Calcd for $C_{17}H_{31}NOP_2Si_2$: C, 53.23; H, 8.15; N, 3.65. Found: C, 52.86; H, 8.08; N, 3.61.

Crystal Data and Summary of Data Collection Parameters for 10: [20] diffractometer Siemens P4; radiation Mo Kα; M = 383.55 g/mol; monoclinic $P2_1$; a = 9.4793(11) Å, b = 10.3843(10) Å, c = 11.5943(11) Å; β = 91.408(8)°; V = 1141.0(2) Å^3; Z = 2; d_{calcd} = 1.116 g/cm^3; Θ range 1.76−28.99°; structure solution by direct methods (SHELXS-86[32]), structure refinement by full-matrix least-squares (SHELXL-93[33]) against F^2; number of reflections collected 4216, number of observed reflections 3497; R = 0.0436, w_R = 0.0997.

General Procedure for the Preparation of the 1-Methylene-1,2-dihydro-1,2-diphosphetes 12a−d. A stirred solution of **7a** (0.22 g, 0.6 mmol) in 5 mL of toluene was treated dropwise at −78 °C (for **12a**−**c**) or −30 °C (for **12d**), respectively, with a solution of **11a**, **11b**, **11c**, or **11d** (0.6 mmol) in 3 mL of toluene, in the course of which the color of the mixture changed from yellow to deep red. The reaction mixture was stirred for 1 h at the same temperature and subsequently allowed to warm to rt. After evaporation of the solvent in vacuo, the residue was taken up in *n*-pentane, filtered through a glass D3 sinter filled to a depth of 3 cm with Celite, and washed twice with a small amount of *n*-pentane. Evaporation of the solvent under vacuum provided the spectroscopically pure products **12a**−**d**.

Dimethyl 2-[1-[bis(trimethylsilyl)methylene]-3-(dimethylamino)-2-phenyl-1,2-dihydro-1,2-diphosphetyl-]maleate (12a): deep red, viscous oil (0.25 g, 82%); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −4.5 (d, $J_{P,P}$ = 113.0 Hz), 23.3 (d, $J_{P,P}$ = 113.0 Hz); ^1H NMR (CD_2Cl_2) δ 0.13 (s, 18H), 2.87 (s, 6H), 3.50 (s, 3H), 3.52 (s, 3H), 4.94 (dd, $J_{H,P}$ = 14.0, 10.0 Hz, 1H), 6.16 (d, $J_{H,P}$ = 18.1 Hz, 1H), 7.33−7.43 (m, 5H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 4.8 (d, $J_{C,P}$ = 4.8 Hz), 4.9 (s), 10.8 (dd, $J_{C,P}$ = 42.6, 10.4 Hz), 41.0 (s), 51.6 (s), 51.9 (s), 95.1 (dd, $J_{C,P}$ = 89.9, 24.9 Hz), 128.4 (dd, $J_{C,P}$ = 6.4, 2.4 Hz), 128.9 (s), 129.8 (d, $J_{C,P}$ = 5.6 Hz), 132.4 (dd, $J_{C,P}$ = 41.0, 8.8 Hz), 133.3 (dd, $J_{C,P}$ = 19.3, 3.2 Hz), 146.8 (dd, $J_{C,P}$ = 44.2, 7.2 Hz), 159.5 (dd, $J_{C,P}$ = 24.9, 3.2 Hz), 164.5 (d, $J_{C,P}$ = 17.7 Hz), 165.2 (d, $J_{C,P}$ = 10.4 Hz); IR (CCl_4) 2951, 1725 (C=O) cm^{-1}; MS (EI, 70 eV) *m*/*z* (rel int) 509 (11, M^+). Anal. Calcd for $C_{23}H_{37}NO_4P_2Si_2$: C, 54.24; H, 7.32; N, 2.75. Found: C, 53.79; H, 7.31; N, 2.57.

Diethyl 2-[1-[bis(trimethylsilyl)methylene]-3-(dimethylamino)-2-phenyl-1,2-dihydro-1,2-diphosphetyl]maleate (12b): deep red, viscous oil (0.26 g, 82%); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −3.9 (d, $J_{P,P}$ = 113.5 Hz), 23.0 (d, $J_{P,P}$ = 113.5 Hz); ^1H NMR (C_6D_6) δ 0.52 (s, 18H), 0.91 (t, $J_{H,H}$ = 7.1 Hz, 3H), 1.04 (t, $J_{H,H}$ = 7.1 Hz, 3H), 2.20 (s, 6H), 3.87 (q, $J_{H,H}$ = 7.1 Hz, 2H), 4.01 (dq, $J_{H,P}$ = 2.0 Hz, $J_{H,H}$ = 7.1 Hz, 2H), 4.87 (dd, $J_{H,P}$ = 14.0, 10.2 Hz, 1H), 6.23 (d, $J_{H,P}$ = 18.4 Hz, 1H), 7.03−7.17 (m, 4H), 7.41−7.45 (m, 1H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 5.7 (d, $J_{C,P}$ = 4.6 Hz), 5.8 (s), 11.0 (dd, $J_{C,P}$ = 42.7, 9.9 Hz), 14.0 (s), 40.0 (s), 60.7 (s), 61.1 (s), 95.4 (dd, $J_{C,P}$ = 89.6, 24.8 Hz), 128.3 (d, $J_{C,P}$ = 6.7 Hz), 129.6 (s), 130.2 (d, $J_{C,P}$ = 5.3 Hz), 133.3 (dd, $J_{C,P}$ = 41.4, 9.2 Hz), 133.6 (dd, $J_{C,P}$ = 19.1, 2.7 Hz), 146.8 (dd, $J_{C,P}$ = 47.3, 7.6 Hz), 159.8 (dd, $J_{C,P}$ = 25.1, 3.3 Hz), 164.0 (d, $J_{C,P}$ = 10.7 Hz), 164.8 (d, $J_{C,P}$ = 18.3 Hz); IR (CCl_4) 1733 (C=O) cm^{-1}; MS (EI, 70 eV) *m*/*z* (rel int) 537 (4, M^+). Anal. Calcd for $C_{25}H_{41}NO_4P_2Si_2$: C, 55.88; H, 7.69; N, 2.61. Found: C, 55.00; H, 7.46; N, 2.76.

Di-*tert*-butyl 2-[*trans*-1-[bis(trimethylsilyl)methylene]-3-(dimethylamino)-2-phenyl-1,2-dihydro-1,2-diphosphetyl]maleate (12c): deep red crystals (0.26 g, 74%); mp 113 °C; $^{31}P\{^1H\}$ NMR (C_6D_6) δ −4.0 (d, $J_{P,P}$ = 121.8 Hz), 25.2 (d, $J_{P,P}$ = 121.8 Hz); ^1H NMR (C_6D_6) δ 0.50 (s, 18H), 1.27 (s, 9H), 1.48 (s, 9H), 2.17 (s, 6H), 4.83 (dd, $J_{H,P}$ = 13.9, 11.0 Hz, 1H), 5.89 (d, $J_{H,P}$ = 19.5 Hz, 1H), 7.00−7.16 (m, 4H), 7.40−7.45 (m, 1H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 5.9 (d, $J_{C,P}$ = 4.6 Hz), 6.0 (s), 14.3 (dd, $J_{C,P}$ = 41.4, 10.4 Hz), 28.0 (s), 28.3 (s), 40.6 (s), 80.8 (s), 82.0 (s), 96.7 (dd, $J_{C,P}$ = 88.7, 27.7 Hz), 128.8 (d, $J_{C,P}$ = 4.8

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Hz), 129.3 (s), 132.2 (d, $J_{C,P}$ = 6.4 Hz), 133.8 (dd, $J_{C,P}$ = 19.3, 2.4 Hz), 134.5 (dd, $J_{C,P}$ = 43.1, 9.2 Hz), 144.9 (dd, $J_{C,P}$ = 52.2, 7.2 Hz), 160.2 (dd, $J_{C,P}$ = 25.7, 4.0 Hz), 163.3 (d, $J_{C,P}$ = 20.1 Hz), 164.2 (d, $J_{C,P}$ = 8.8 Hz); IR (CCl_4) 1723 (C═O) cm^{-1}; MS (EI, 70 eV) *m/z* (rel int) 593 (20, M^+). Anal. Calcd for $C_{29}H_{49}NO_4P_2Si_2$: C, 58.65; H, 8.32; N, 2.36. Found: C, 57.65; H, 8.17; N, 2.02.

Crystal Data and Summary of Data Collection Parameters for 12c:[20] diffractometer Siemens P4; radiation Mo Kα; M = 592.80 g/mol; triclinic $P\bar{1}$; a = 10.839(2) Å, b = 11.379(2) Å, c = 15.578(3) Å; α = 78.96(3)°, β = 74.87(3)°, γ = 79.54(3)°; V = 1802.8(6) Å^3; Z = 2; d_{calcd} = 1.094 g/cm^3; Θ range 1.37−22.50°; structure solution by direct methods (SHELXS-86[32]), structure refinement by full-matrix least-squares (SHELXL-93[33]) against F^2; number of reflections collected 5608, number of observed reflections 4709; R = 0.0655, w_R = 0.1150.

***(E)*-*tert*-Butyl 3-[1-[bis(trimethylsilyl)methylene]-3-(dimethylamino)-2-phenyl-1,2-dihydro-1,2-diphosphetyl]acrylate (12d):** deep red, viscous oil (0.23 g, 78%); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −7.5 (d, $J_{P,P}$ = 104.2 Hz), 24.4 (d, $J_{P,P}$ = 104.2 Hz); ^1H NMR (C_6D_6) δ 0.53 (s, 18H), 1.35 (s, 9H), 2.31 (s, 6H), 4.76 (dd, $J_{H,P}$ = 15.4, 11.9 Hz, 1H), 6.66 (dd, $J_{H,P}$ = 19.0 Hz, $J_{H,H}$ = 16.2 Hz, 1H), 7.08 (dd, $J_{H,P}$ = 2.0 Hz, $J_{H,H}$ = 16.2 Hz, 1H), 7.13−7.19 (m, 3H), 7.33−7.38 (m, 2H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 5.6 (s), 11.0 (dd, $J_{C,P}$ = 40.0, 12.1 Hz), 27.9 (s), 38.0 (s), 80.3 (s), 92.1 (dd, $J_{C,P}$ = 89.3, 27.4 Hz), 128.5 (s), 128.8 (d, $J_{C,P}$ = 9.0 Hz), 129.1 (d, $J_{C,P}$ = 8.1 Hz), 132.2 (d, $J_{C,P}$ = 17.1 Hz), 135.3 (dd, $J_{C,P}$ = 35.5, 7.6 Hz), 141.9 (dd, $J_{C,P}$ = 67.8, 13.9 Hz), 160.1 (dd, $J_{C,P}$ = 23.3, 6.7 Hz), 164.1 (d, $J_{C,P}$ = 21.5 Hz); IR (CCl_4) 1724 (C═O) cm^{-1}; MS (EI, 70 eV) *m/z* (rel int) 493 (46, M^+). HRMS calcd 493.2151, found 493.2148.

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Supporting Information Available: Preparation procedures (**3c**), NMR peak assignments (**3c**, **4**, **7a**−**c**, **8**−**10**, **12a**−**d**), ^1H NMR spectra (**3c**, **4**, **7c**, **10**, **12b**−**c**), $^{13}C\{^1H\}$ NMR spectra (**3c**, **4**, (*E*)-**7a**, (*Z*)-**7a**, **7c**, **9**, **10**, **12b**−**d**), and ^{13}C NMR spectra (**7a**) (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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