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[4+2] CYCLOADDITION REACTIONS OF TRIARYLPHOSPHAALKENES

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Abstract - Cycloaddition reactions of mesityl(diphenylmethylene)phosphine (1) were investigated. With several dienes, no Diels-Alder reactions were observed. With azides, diphenyldiazomethane and 2,4,6-trimethylbenzonitrile oxide, the corresponding cycloadducts (4, 12, 17, 20) were obtained. In the case of phenyl azide, a competing Staudinger reaction occurred leading to 3.

INTRODUCTION

Mesityl(diphenylmethylene)phosphine 1 is a thermally stable phosphaalkene.[1,2] Its structure was originally assigned on the basis of spectral data and has meanwhile been confirmed by X-ray structure determination of 1 and of two metal complexes.[3,4] From these data, and from the instability of less substituted derivatives it was concluded[2] that 1 contains an essentially localized P=C bond and owes its thermal stability mainly to steric protection of the double bond.

So far, the chemical reactivity of phosphaalkenes has not received much attention.[5] Polar compounds may add to the P=C bond; the regiochemistry of these additions is such that phosphorus acts as the positive end of the dipole. However, even towards small molecules such as water or ethanol, the reactivity is low and needs acid or base catalysis.[2] Similarly, phosphaalkenes react rather slowly with oxygen and other oxidizing reagents,[6,7] and with methyl iodide.[8] It was of interest to investigate the behaviour of the P=C bond in phosphaalkenes in cycloaddition reactions and to compare it with that of two analogous systems, i.e. the C=N bond in imines[9] and the P=N bond in iminophosphines.[10]

RESULTS AND DISCUSSION

Attempted Diels-Alder reactions

We found that 1 is quite unreactive in attempted Diels-Alder reactions with a variety of electron-rich or electron-poor dienes. With 2,3-dimethylbutadiene, cyclopentadiene, tetrachloro-α-pyron and 5-carbomethoxy-α-pyron, the starting materials were recovered unchanged even after prolonged heating to 80-150°C. Acroleine (80°C) and 2,3-dicarbomethoxybutadiene (either at 122°C; or at room temperature in the presence of boron trifluoride etherate) decomposed under the reaction conditions, whereas 1 decomposed on treatment with hexachlorocyclopentadiene and 1,3-diphenylisobenzofuran. A defined adduct was never observed.

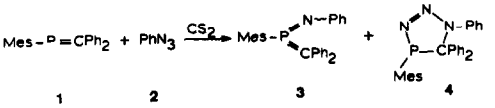
In the literature, Diels-Alder reactions of heterosubstituted[11,12] and cyclic[12,13] phosphaalkenes have been reported. Very likely, steric hindrance is a major cause of the non-reactivity of 1, although additional electronic factors cannot be excluded at the present time.

Reactions with azides

In contrast to the lack of (clean) reactions with dienes, cycloaddition products of triarylphosphaalkenes could be obtained with 1,3-dipoles.

Phenyl azide (2) added slowly to 1. The course of the reaction was strongly solvent dependant. In boiling benzene or in chloroform a fast reaction (1 h) gave the iminomethylenephosphorane 3 as the only product. However, in CS_2 (80°C, 24 h, sealed ampoule), 3 was a minor byproduct, and the cyclo-adduct 4 was obtained in about 90% yield (Scheme 1).

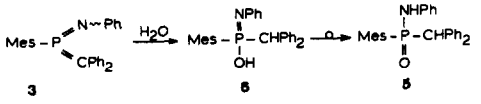
scheme 1



Mes = 2,4,6-trimethylphenyl

The structure of 3 was assigned unequivocally by its spectral data and by its conversion to 5 by water. There are two possible mechanisms for this reaction, starting either by protonation of 3 on nitrogen or on carbon. Contrary to imines, which are readily methylated on nitrogen by methyl iodide,[9] 3 did not react with methyl iodide at all. We therefore assume that primary attack of the proton occurs at the ylidic carbon atom, followed by, or concerted with, addition of a hydroxyl group equivalent at phosphorus to furnish 6 which rearranges to 5 (Scheme 2).

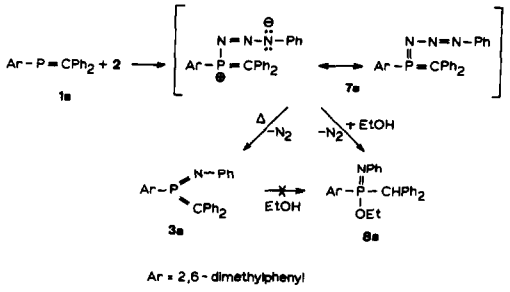
scheme 2



Furthermore, 3 is characterized as a methylenephosphorane by its ^{31}P chemical shift (one signal at δ = 18.8 ppm) and by two signals of the ylidic carbon atoms (δ = 68.7 and 68.3 ppm; both $^{1}J(PC)$ = 166.5 Hz). Obviously, 3 is a mixture of the Z- and the E-isomers (approximately 1:1). The NMR data show the expected analogy with those of aminoiminomethylenephosphoranes prepared along a different route by Niecke and Wildbredt;[14] in particular, the ^{13}C signals of the amino analogues (δ = 75-90 ppm; $^{1}J(PC)$ = 207-216 Hz) are typical, while the ^{31}P resonances are shifted to lower field due to the inductive effect of the amino substituent.

Compound 3 is obviously the product of a Staudinger reaction.[15] This reaction is believed to proceed by a two-step mechanism: in the first step, there is a nucleophilic attack of the phosphine on the terminal nitrogen of the azide, leading to a phosphazide, in our case 7 (Scheme 3); the second step consists of ring closure and extrusion of N_2, in this case leading to 3. Depending on the nature of the phosphine both steps can be rate determining. As we had observed that with certain phosphaalkenes the second step is the slow one,[16] it was conceivable that the short-lived intermediate 7 could be intercepted, thus proving its involvement. Ethanol seemed to be a suitable reagent for this purpose, as it was expected to react rapidly with the zwitterionic 7, while 3 was found to be inert towards boiling ethanol. Indeed, when the reaction between 1a, the lower homologue of 1, and 2 was performed in boiling ethanol, the iminophosphinate 8a was obtained instead of 3a, together with some 5a. Compound 8a could not be obtained in analytically pure form, nor could it be hydrolyzed to the corresponding phosphinic acid;[6] however, it was fully identified by its NMR spectra and its exact mass spectrum.

scheme 3



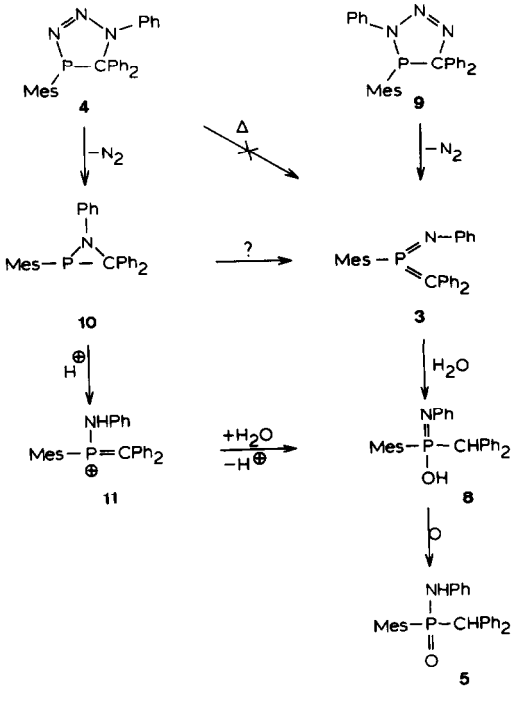
Ar = 2,6-dimethylphenyl

The structure assignment of the second product from 1 and 2, the cyclo-adduct 4, was much more difficult and cannot be considered fully settled at this moment. Our preference for structure 4 above that of the regioisomer 9 (Scheme 4) is based on the following evidence.

Compound 4 was not stable enough to obtain an analytically pure sample; on exposure to air or column chromatography, it decomposed to several other compounds (^{31}P-NMR), of which 5 could be isolated in low yield (21%). At first sight, it might appear as if the con-

version of 4 to 5 could be most easily explained from structure 9 by invoking the intermediacy of 3 (Scheme 4). However, this course of events is not likely as the cyclo-adduct, once formed, was not transformed to 3. On the other hand, there are several conceivable pathways from 4 to 5 (Scheme 4). For instance, loss of N_2 from 4 might lead to 10 which, by opening of the strained three-numbered ring, could lead to 3 and further to 8 and 5; alternatively, proton catalysis may, under circumvention of 3, lead to 8 (and 5) via 11. Thus, the conversion of 4 to 5 does furnish partial information concerning the structure of 4, but it is not helpful in distinguishing between the structures 4 and 9.

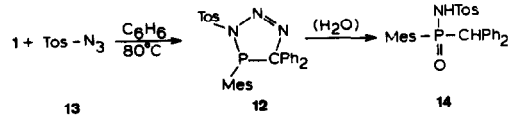
scheme 4



More decisive is the NMR spectroscopic evidence, keeping in mind that ^{31}P chemical shifts of this type of cyclic compounds are not well understood nor predictable.[17] Though close models for 4 are lacking, structure 9 is definitely not in accord with the surprisingly low ^{31}P chemical shift of δ = 140.8 ppm; aminophosphines of comparable structure usually have resonances at much higher field[18] (e.g. $MesP(CHPh_2)NEt_2$, $\delta(^{31}P)$ = 64.5 ppm[2]).

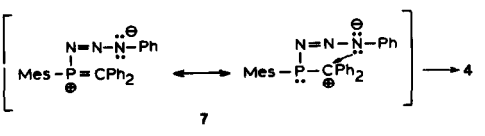
Finally, structure 9 for the cyclo-adduct from 1 and 2 is strongly contraindicated by the structure of the cyclo-adduct 12 obtained from the reaction between 1 and tosyl azide (13) (Scheme 5). Compound 12 has a 4,5-dihydro-1,2,3,4-triazaphosphole structure analogous to 9 and regioisomeric with 4, as evidenced by its NMR data, in particular $\delta(^{31}P)$ = 98.8 ppm. Exposure of 12 to (moist) air gave 14, presumably by the mechanism discussed for the (assumed) transformation of 9 to 5. The formation of 12 was not solvent dependant: both in CS_2 and in benzene, 12 was the only identifiable product; an iminomethylenephosphoran 15 analogous to 3 was not observed.

scheme 5



The formation of cyclo-adducts with opposite regiochemistry in the reaction of 1 with the closely related azides 2 and 13 needs some comment. Both may be concerted 1,3-dipolar addition reactions, in which case the regiochemistry must be a consequence of differences in steric, polar and frontier orbital effects between the two 1,3-dipoles. However, the simultaneous formation of 3 and 4 may also be explained by assuming a different genesis, i.e. the Staudinger reaction which apparently does not occur with 13, as no iminomethylenephosphorane 15 was observed. With 13, the product of the first step is 7 (Scheme 3) which in part loses N_2 to give 3. An alternative reaction mode, not available to normal tertiary phosphines, is ring closure to 4 (Scheme 6). Thus, the difference in regiochemistry would be a consequence of two completely different mechanisms, only 12 being a genuine concerted 1,3-dipolar cyclo-adduct, while 4 is the product of two-step, Staudinger-type reaction.

scheme 6

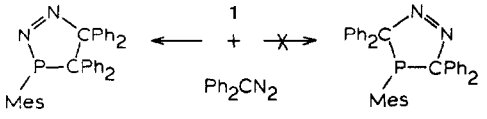


In the literature, reactions of a P=C bond incorporated into 1,2,3-diazaphosphole systems with phenyl azide have been reported.[19] Depending on the substitution pattern, a Staudinger type product (analogous to 3) or a trimer derived thereof were obtaind.

Reaction with diphenyldiazomethane

The reaction of 1 with diphenyldiazomethane (16) in boiling cyclohexane was completed after 24 h. On crystallization from pentane, 67% of the cyclo-adduct 17 were obtained (Scheme 7). The structure of 17 follows unequivocally from the NMR spectra. Diagnostic is the $\delta(^{31}P)$ = 47.4 ppm;[16b] the regioisomer 18 of 17 is a tertiary phosphine and is expected to have a chemical shift at higher field. Even more compelling is the nonequivalence of the carbon atoms of the diazophosphole ring (C(4) : δ = 48.0 ppm, $^{1}J(PC)$ = 15 Hz; C(5): δ = 64.4 ppm, $^{2}J(PC)$ = 22 Hz); in 18, they must be equivalent.

scheme 7



17 16 18

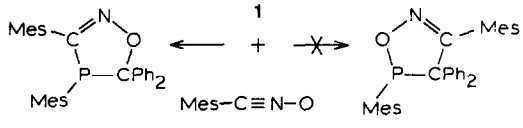
On the NMR time scale, the rotation around the P-mesityl bond of 17 is slow, as the ortho-methyl groups (^{13}C; ^{1}H) and the two aromatic protons of the mesityl group are nonequivalent. Presumably, the steric hindrance of the mesityl group is considerably increased by a buttressing effect of the two phenyl groups on C(5) on those on C(4).

The reactions of diazoalkanes with the P=C bond of 1,2,3-diazaphospholes has received considerable attention. In most cases, extrusion of N_2 occurred, leading to trimeric products,[20] to 1:2 adducts,[21] or, with 16, to a phosphirane.[12,22] Only in the case of diazafluorene, a nitrogen-retaining cycloadduct was isolated.[20] The structure assigned to this cycloadduct would imply a regiochemistry of the addition which is opposite to that for 1.

Reaction with 2,4,6-trimethylbenzonitrile oxide

The reaction of 1 with 2,4,6-trimethylbenzonitrile oxide (19) in cyclohexane or in ethanol was fast (< 0.5 h) at room temperature and gave the cyclo-adduct 20 quantitatively (Scheme 8). The structure of 20 can be distinguished from that of its regioisomer 21 by the NMR data. The phosphorus chemical shift (δ = 9.3 ppm) is typical for a (negatively substituted) tertiary phosphine (20) and not for a phosphinous ester (21). The parameters for C(3) (δ = 160.6 ppm, $^{1}J(PC)$ = 45 Hz) and C(5) (δ = 98.8 ppm, $^{1}J(PC)$ = 30 Hz) support the structural assignment. Attempts to further characterize 20 by chemical transformations failed. With 1N KOH, S_8, 6N HCl/EtOH (1:1), no reaction occurred; with H_2O_2, six unidentified phosphorus compounds were formed (^{31}P NMR). After reaction with aqueous bromine, 61% benzophenone was isolated by TLC.

scheme 8



20 19 21

One of the mesityl groups of 20 shows hindered rotation in the ^{1}H-NMR spectrum. It was identified as the P-mesityl group by the observation of phosphorus coupling on one of the two ortho-methyl groups at 250 MHz and room temperature (δ = 2.49 ppm, $w_{\frac{1}{2}}$ = 8 Hz). In the 90 MHz spectrum, coalescence occurred at 314.5 K; the rotation barrier is $\Delta G^{\ddagger}$ = 16 kcal.mol^{-1}.

The same regiochemistry as for 1 has been observed for the reaction of a nitrile oxide with the P=C bond of a 1,2,3-diazaphosphole system.[23] and for the comparable reaction of a nitrile imine.[24] Remarkably, the reaction of a nitrile oxide with the corresponding diazaarsazol gave the same regioisomer as the kinetic product at low temperature while at room temperature, the other regioisomer was obtained as the thermodynamically favoured product.[23] This illustrates the delicate balance of different effects (vide infra).

CONCLUSION

The reaction of 1 with organic azides, diphenyldiazomethane and mesitylnitrile oxide

leads to the formation of cyclo-adducts. The regiochemistry of these reactions is not easily and unequivocally explained, as in 1 the HOMO (σ; lone pair at phosphorus) and NHOMO (π; P=C double bond) are very close in energy[2,25] so that besides frontier orbital controle, polar effects and especially steric factors may be important, as 1 is a rather crowded molecule. Further results are therefore required to discuss these factors in a meaningful way and to compare the behaviour of the phosphaalkenes with that of related compounds. The lack of reactivity of 1 in Diels-Alder reactions is probably caused by steric hindrance at the P=C bond.

EXPERIMENTAL

Melting points are uncorrected. Mass spectra were recorded on a Varian MAT CH-5 mass spectrometer with electron impact at 70eV or on a Varian MAT 711 by the field desorption method. NMR spectra were recorded on a Bruker WH 90 or WM 250 spectrometer. ^1H Chemical shifts are given in δ(ppm) from internal TMS; ^{13}C chemical shifts are given in δ(ppm) from TMS with the solvent peaks as internal standard; ^{31}P chemical shifts are given in δ(ppm) from external 85% H_3PO_4. Positive shifts are downfield in all cases. The IR spectra were recorded on a Perkin-Elmer 580B spectrophotometer; frequencies are given in cm^{-1}. Elemental analyses were performed at the Microanalytical Department of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands. All solvents were distilled under argon and were oxygen free.

Attempted Diels Alder reactions

In view of the negative results of these experiments, only reaction conditions, products and their identification are indicated in an abbreviated form.

2,3-Dimethylbutadiene (22). -1 (ca. 10 mg, 0.03 mmol), 22 (ca. 7 µl, 0.085 mmol). C_6D_6, 32 h, 140°C, in a sealed tube. Products (^1H NMR): 1, 22 and poly-22.

Cyclopentadiene (23). -1 (ca. 10 mg, 0.03 mmol), 23 (ca. 7 µl, 0.085 mmol), C_6D_6, 30 h, 100-150°C in a sealed tube. Products (^1H NMR): 1, 23, and poly-23.

Tetrachloro-α-pyron (24). -1 (102 mg, 0.32 mmol), 24 (75 mg, 0.32 mmol), C_6H_{12}, 18 h, 80°C. Products (^1H NMR): 1 and 24.

5-Carbomethoxy-α-pyron (25). -1 (138.7 mg, 0.44 mmol), 25 (67.8 mg, 0.44 mmol), toluene, 18 h, 100°C. Products (^1H NMR): 1 and 25.

Acroleine (26). -1 (351 mg, 1.11 mmol), 26 (freshly distilled, 72 µl, 1.1 mmol), C_6H_{12}, 18 h, 80°C. Products (^1H NMR): 1, and (little) 26.

2,3-Dicarbomethoxybutadiene (27). - NMR experiment with excess of 1 over 27, $CDCl_3$, 2 h, 120° in a sealed tube. Products (^1H NMR): 1; 27 had disappeared.

Hexachlorocyclopentadiene (28). -1 (294 mg, 0.93 mmol), 28 (0.16 µl, 1 mmol, freshly distilled), toluene, 25°C, 300 h (black/purple colour appeared instantaneously). Products (^1H, ^{31}P NMR): $MesPCl_2$[26] (δ(^{31}P) = 168.2 ppm), Ph_2CH_2.

1,3-Diphenylisobenzofuran (29). -1 (57.4 mg, 0.18 mmol), 29 (48.9 mg, 0.18 mmol), toluene, 40 h, 100-150°C. Products (^1H, ^{31}P NMR): No 1, but $MesPH(=O)CHPh_2$ (δ(^{31}P) = 24.6 ppm)[2] which is probably formed by contact with (moist) air; 29 and several unidentified products (^{31}P).

E- and Z-(Phenylimino)(diphenylmethylene)(2,4,6-trimethylphenyl)phosphorane (3).

Compound 1 (33.6 mg, 0.11 mmol) and 2 (16 mg, 0.13 mmol) were dissolved in chloroform and heated at 100° in a sealed tube for 1 h. According to ^{31}P NMR, 3 was the only compound present. ^1H NMR (C_6D_6) δ 1.80 (s, 6H, o-CH_3), 1.82 (s, 3H, p-CH_3), 6.46 (bs, 2H, Mes-H), 6.56-7.33 (m, 11H, Ph-H), 7.51-7.78 (m, 2H, Ph-H), 7.78-8.00 (m, 2H, Ph-H). ^{31}P NMR (C_6D_6): δ 18.8. ^{13}C NMR (C_6D_6) δ 21.0 (s, p-CH_3), 26.3 (s, o-CH_3), 68,26 (d, $^1J_{PC}$ = 166, ylid-C), 68.32 (d, $^1J_{PC}$ = 166.5, ylid-C), 119.6-130.7 (m, Ar-C), 140.4-145.8 (m, Ar-C). m/z (FD): 407[M^+]. The reaction mixture was exposed to air for 48 h and evaporated. Column chromatography (silicagel, $CHCl_3$) gave pure 5 according to ^1H NMR spectroscopy (40 mg, 86%).

4,5-Dihydro-1,5,5-triphenyl-4-(2,4,6-trimethylphenyl)-1,2,3,4-triazaphosphole (4).

Compound 1 (270.5 mg, 0.856 mmol) was dissolved in CS_2 (5 mL) and 2 (102 mg, 0.86 mmol) was added. The mixture was heated in a sealed tube at 80°C for 24 h. The dark green solution was evaporated and the oily residue dissolved in C_6D_6. ^1H NMR (C_6D_6) (4) δ 1.66 (s, 3H, p-CH_3), 2.33 (d, $^4J_{PH}$ = 2, 6H, o-CH_3), 6.24 (d, $^4J_{PH}$ = 4.5, 2H, Mes-H), 6.37-7.04 (m, 13H, Ph-H), 7.76-7.97 (m, 2H, Ph-H). ^{31}P NMR (C_6D_6) (4) 140.8 (92%), (3) 18.8. ^{13}C NMR (C_6D_6) (4) δ 21.4 (s, p-CH_3), 23.1 (d, $^3J_{PC}$ = 7.4, o-CH_3), 61.1 (d, $^1J_{PC}$ = 49.9, C(5)), 126-132 (m, Ar-C), 138-143 (m, Ar-C).

N-Phenyl-(diphenylmethyl)(2,4,6-trimethylphenyl)phosphinamide (5).

The reaction mixture obtained from 1 and 2 as described for 4 (400 mg product containing 92% 4, 0.85 mmol) was exposed to air. Column chromatography (silicagel) yielded the following fractions: with C_6H_6 200 mg (according to TLC: 5 unidentified compounds); with $CHCl_3$ 100 mg of a red solid which, on crystallization from pentane gave colourless crystals of pure 5 (76.1 mg, 21%), m.p. 200-201°C. ^1H NMR ($CDCl_3$) 2.24 (s, 3H, p-CH_3), 2.41 (d, $^4J_{PH}$ = 1.5, 6H, o-CH_3), 4.53 (d, $^2J_{PH}$ = 12, 1H, methine-H), 4.83 (d, $^2J_{PH}$ = 10, 1H, N-H), 7.87-6.79 (m, 17H, Ar-H). ^{31}P NMR ($CDCl_3$) 25.0. IR (KBr) · 3220; 3190 (N-H), 1600 (C=C, Ph), 1500 (P-Ph), 1280 (N-Ph), 1230 cm^{-1} (P=O). m/z (relative intensity) 425 (4) $[M]^+$, 332 (9) $[M-PhNH_2]^+$, 258 (23) $[M-Ph_2CH]^+$, 182 (64) $[Ph_2C=O]^+$, 167(100) $[Ph_2CH]^+$. HRMS Calc ($C_{28}H_{28}NOP^+$), 425.1385. (Found: 425.1389). Found: C, 78.01; H, 6.67; N, 3.13. $C_{28}H_{28}NOP$ (MW = 425.48) requires: C, 78.97; H, 6.63; N, 3.29%.

Ethyl N-Phenyl-(diphenylmethyl)(2,6-dimethylphenyl)phosphiniminate (8a).

Compound 1a (151 mg, 0.50 mmol) was dissolved in ethanol (15 mL) and 2 (60 μL, 0.50 mmol) was added. After heating under reflux for 1 h a ^{31}P NMR spectrum of a sample indicated that the reaction had consumed the starting materials for ca. 60%. The solution was heated for another 2.5 h and evaporated to dryness. The oily residue (206 mg) was dissolved in benzene (10 mL) and pentane (10 mL) was added dropwise whereupon a precipitate formed which, according to a ^{1}H NMR spectrum, consisted of pure 5a (49.5 mg, 24%). ^{1}H NMR ($CDCl_3$) δ 2.44 (d, $^{4}J_{PH}$ = 1.5, 6H, o-CH_3), 4.51 (d, $^{2}J_{PH}$ = 12, 1H, methine H), 4.84 (bd, $^{2}J_{PH}$ = 10, 1H, NH), 6.64-7.56 (m, 16H, Ar-H), 7.73-7.93 (m, 2H, 2H, Ar-H). ^{31}P NMR ($CDCl_3$) δ 25.4. The mother liquor was evaporated; the oily residue consisted of 8a (152.5 mg, 69%). ^{1}H NMR ($CDCl_3$) δ 0.91 (t, $^{3}J_{PH}$ = 7, 3H, CH_2CH_3), 2.29 (s, 6H, o-CH_3), 3.36-4.04 (m, 2H, CH_2CH_3), 4.47 (d, $^{2}J_{PH}$ = 18, 1H, methine-H), 6.64-7.62 (m, 15H, Ar-H), 7.87-8.01 (m, 2H, Ar-H). ^{31}P NMR ($CDCl_3$) δ 25.7. m/z (relative intensity) 439 (100) $[M]^+$, 410 (15) $[M-C_2H_5]^+$, 302 (21) $[M-PhN-EtOH]^+ \equiv [1]^+$, 272 (39) $[M-CHPh]^+$ 244 (59) $[M-CHPh_2-C_2H_4]^+$, 167 (38) $[CHPh_2]^+$. HRMS Calc ($C_{20}H_{30}NOP^+$), 439.2066. (Found: 439.2065). An attempt to react 8a with water failed. 8a (151 mg, 0.34 mmol) was dissolved in THF (10 mL) and water (0.40 mL) was added. After stirring for 3 h the solvent was evaporated, the residue was extracted with pentane (50 mL); evaporation of the pentane solution yielded 146 mg of unchanged 8a as an oil, according to a ^{1}H NMR spectrum. Purification of 8a by TLC (silicagel, $CHCl_3$) failes, giving only 5a and benzophenone as identifiable products.

4,5-Dihydro-5,5-diphenyl-4-(2,4,6-trimethylphenyl)-3-p-toluenesulfonyl-3H-1,2,3,4-triazaphosphole (12) and N-p-Toluenesulfonyl-(2,4,6-trimethylphenyl-(diphenylmethyl)phosphinamide (14)

Compound 1 (52 mg, 0.16 mmol) and 13 were dissolved in benzene (0.6 mL) and stirred for 2.5 h at room temperature. Evaporation to dryness yielded 12 as a resin; according to NMR spectroscopy, it was pure. Attempts to crystallize 12 from cyclohexane or pentane failed. ^{1}H NMR (C_6D_6) δ 1.78 (s, 3H, p-CH_3 of Mes), 1.96 (s, 3H, p-CH, of Tos), 2.46 (d, $^{4}J_{PH}$ = 2.3, 6H, o-CH_3), 6.37 (d, $^{4}J_{PH}$ = 5, 2H, Mes-H), 6.67-7.12 (m, 12H, Ar-H), 7.80-7.97 (m, 2H, Tos-o-H). ^{31}P NMR (C_6D_6) δ 98.8. ^{13}C NMR (C_6D_6) δ 21.1, 21.2 (2s, 2p-CH_3) 23.2 (d, $^{3}J_{PC}$ = 6.1, o-CH_3), 55.1 (d, $^{1}J_{PC}$ = 79, C(5)), 123.2-145.7 (m, Ar-C). Exposure of the NMR solution of 12 to air gave almost pure 14 according to ^{1}H NMR spectroscopy. Attempts to crystallize 14 from cyclohexane failed. ^{1}H NMR (14, C_6D_6) δ 1.87 (s, 3H, p-CH_3 of Tos) 1.92 (d, $J_{PH} \approx 0.6$, 3H, p-CH_3 of Mes), 2.64 (d, $^{4}J_{PH}$ = 1.2, 6H, o-CH_3), 4.51 (d, $^{2}J_{PH}$ = 11, 1H, methine-H), 5.91 (vbs, 1H, N-H), 6.51-7.26 (m, 12H, Ph-H), 7.46-7.62 (m, 2H, Ph-H), 7.82-7.90 (m, 2H, Tos-o-H). ^{31}P NMR ($CDCl_3$) δ 27.0. m/z (relative intensity) 503 (13) $[M]^+$, 336 (30) $[M-Ph_2CH]^+$, 167 (54) $[PhCH]^+$, 154 (100) $[C_7H_6SO_2]^+$. HRMS Calc ($C_{29}H_{30}NO_3PS^+$): 503.1753. (Found: 503.1760).

4,5-Dihydro-4,4,5,5-tetraphenyl-3-(2,4,6-trimethylphenyl)-3H-1,2,3-diazaphosphole (17).

Compound 1 (383 mg, 121 mmol) and 16 (235 mg, 1.21 mmol) were dissolved in cyclohexane (10 mL) and heated for 24 h at 80° whereafter the typical red colour of 16 had disappeared. The solvent was evaporated and a crystallization from pentane gave 17 as a white powder (408 mg, 67%), m.p. 200-202. An additional crystallization did not further purify 17. ^{1}H NMR (C_6D_6) δ 2.41 (s, 3H, CH_3), 2.70 (s, 3H, CH_3), 3.17 (d, $^{4}J_{PH}$ = 2, 3H, o-CH_3), 6.27 (d, $^{4}J_{PH}$ = 4.7, 1H, Mes-H), 7.21 (d, $^{4}J_{PH}$ = 4.0, 1H, Mes-H), 7.39-7.42 (m, 2H, Ph-H), 7.55-7.99 (m, 14H, Ph-H), 8.29-8.33 (m, 2H, Ph-H), 8.71-8.75 (m, 2H, Ph-H). ^{31}P NMR (C_6D_6) δ 47.4. ^{13}C NMR (C_6D_6) δ 21.1 (s, p-CH_3), 24.0 (d, $^{3}J_{PC}$ = 7.4, o-CH_3), 48.0 (d, $^{1}J_{PC}$ = 14.8, C(4)), 64.4 (d, $^{2}J_{PC}$ = 22.2, C(5)), 126.4-131.7 (m, Ar-C) 139.7-148.3 (m, Ar-C). m/z (FD) 482 $[M-N_2]^+$.

4,5-Dihydro-5,5-diphenyl-3,4-di(2,4,6-trimethylphenyl)-1,2,4-oxazaphosphole (20).

Compound 1a (1.12 g, 3.54 mmol) and 19 (0.57 g, 3.54 mmol) were dissolved in cyclohexane (5 mL) at room temperature. After 20 min, a white precipitate of 20 appeared in the yellow solution and was filtered off (1.10 g, 66%), m.p. 159-166°. One additional crystallization from cyclohexane raised the m.p. to 168-172°. ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.78 (s, 6H, CH_3) 1.93 (bs, 3H, o-CH_3 of P-Mes), 2.18 (s, 6H, CH_3) 2.49 (bs, 3H, o-CH_3 of P-Mes), 6.68 (bs, 4H, Mes-H), 7.11-7.47 (m, 8H, Ph-H), 7.73-7.89 (m, 2H, Ph-H). ^{31}P NMR ($CDCl_3$) δ 9.3. ^{13}C NMR δ 19.5-23.4 (m, CH_3), 98.8 (d, $^{1}J_{PC}$ = 30, C(5)), 126-130 (m, Ph); 137.2-146.1 (m, Ph); 160.6 (d, $^{1}J_{CH}$ = 45, C(3)). m/z (FD): 477 $[M]^+$. Found: C, 80.61; H, 6.95; N, 2.90; P, 6.48. $C_{32}H_{32}NOP$ (MW = 477.56) requires: C, 80.48; H, 6.76; N, 2.93; P, 6.49.

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