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Novel Photochemical Reactions of Phosphonium-Iodonium Ylides: Synthesis of Phosphonium-Substituted Oxazoles

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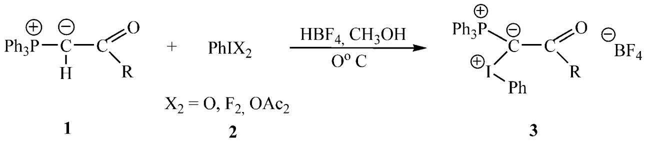
Irradiation of the mixed phosphonium-iodonium ylides **4**–**6** in the presence of acetonitrile, propionitrile, and benzonitrile yielded the oxazole derivatives **9a**–**9c**, **10a**–**10c**, and **11a**–**11c** in 30 %–50 % yields.

Introduction

The work of Wittig et al., especially the discovery of carbonyl olefination by phosphonium ylides[1,2] has spurred development of the chemistry of these species and interest in the properties of other ylides. The first stable aryliodonium ylides were discovered in 1957 on treatment of (difluoroiodo)benzene with dimedone.[3] Since that time the chemistry of iodanes has been considerably developed.[4] Mixed phosphonium ylides were prepared in 1984 by treatment of carbonyl-stabilized phosphonium ylides (e.g., **1**) with λ^3-iodanes such as $Ar(I)Hal_2$, ArIO, or $ArI(OAc)_2$ in the presence of HBF_4 as shown in Scheme 1.[5] The resulting mixed ylides are best described by the resonance structures given below, with a significant contribution from **3d** (Figure 1).[5–7]



Scheme 1.

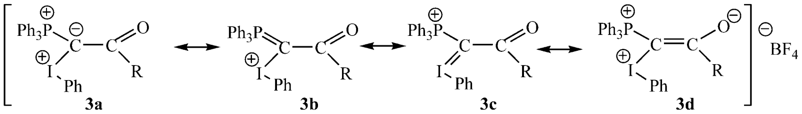
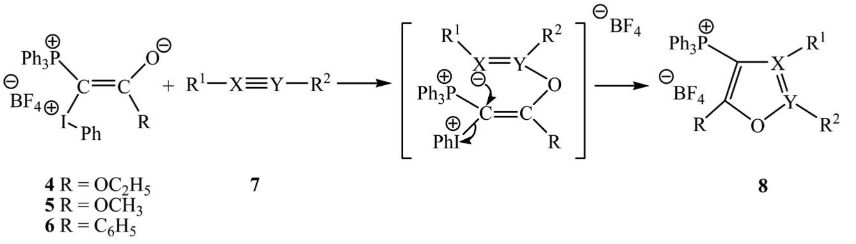


Figure 1. Mesomeric structures of **3**.



Scheme 2.

These resonance formulae show that ylide **3** contains several reaction centers, which represent a molecule with separated charges on the P, I, and O atoms. Analysis of the ylide's structural peculiarities allowed us to conceive the ylides **4**–**6** as possible pseudo 1,3-dipoles for the synthesis

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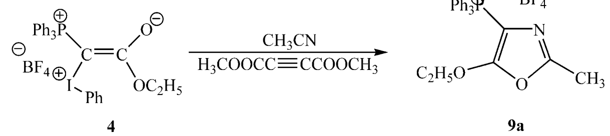
of five-membered heterocycles of type **8** (Scheme 2). In this paper we report the results of our investigations into cycloadditions between the mixed ylides **4**–**6** and triple bonds.

Results

Our experiments involving treatment of **4**–**6** with dimethyl acetylenedicarboxylate (DMAD) as an example of **7** by heating both components with solvents between 20 °C and 65 °C were unsuccessful. However, when we heated **4** and DMAD in acetonitrile as solvent at 80 °C we obtained **9a** in 30% yield (Scheme 3).[8] The product can be explained as arising from **4** by cycloaddition with the C≡N bond.



Scheme 3.

The amazing feature of this process is that no reaction between ylide **4** and acetonitrile was observed in the absence of DMAD. In other words, the DMAD plays the role of a necessary catalyst or a sort of "activator" in this reaction. On the other hand, thermal activation of mixtures of ylides **4**–**6** and acetonitrile gave the corresponding phosphonium salts of the type $Ph_3P^+CH_2COR{\cdot}BF_4^-$ (**12**: R = OC_2H_5, **13**: R = OCH_3, **14**: R = Ph) as side products of decomposition.

This interesting result suggests the following ramifications for future investigation: 1) to find new "activators" and to clarify this phenomenon, and 2) to enlarge the list of compounds of type **7** capable of giving five-membered heterocycles of type **8**. In general, success in these areas promised new ways for the synthesis of polyfunctional oxazoles, which is important because these heterocycles have shown antitumor, antiviral, antibacterial, and antifungal activities.[9–12]

After many experiments with variation of activators (such as diethyl maleate, maleic anhydride, fumaronitrile, vinylene carbonate, etc., which will be described separately), we serendipitously discovered that the process of cycloaddition shown in Scheme 3 can be tremendously accelerated by UV irradiation.

At first we found that the ylide **4** reacts with acetonitrile under irradiation conditions (Hg lamp) to yield **9a** (Scheme 3). The structure of the oxazole **9a** was established by X-ray analysis of single crystals of the product (Figure 2).

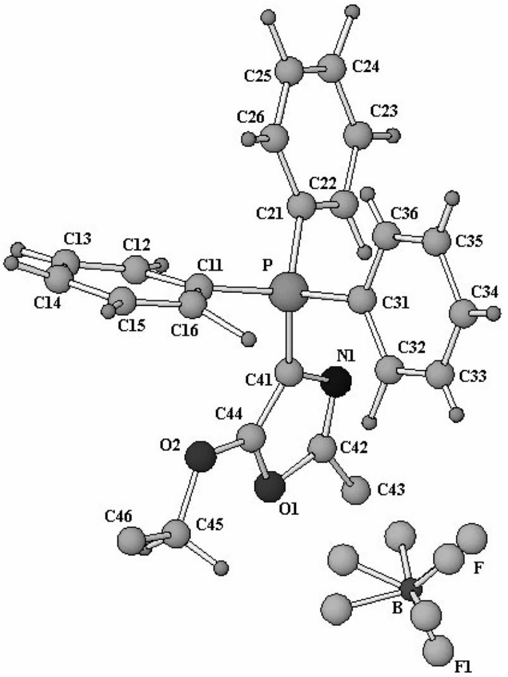
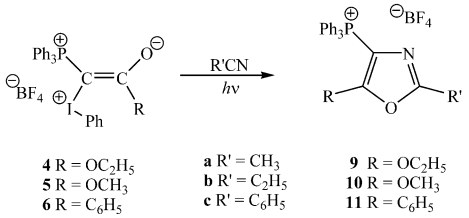


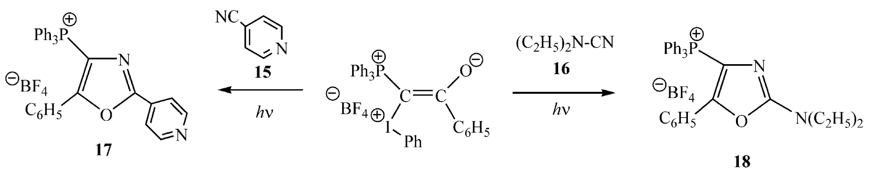
Figure 2. Molecular structure of **9a** in the solid state.

In continuation of our work we found that propionitrile and benzonitrile behave analogously to acetonitrile. Under photochemical conditions with **4** we obtained the oxazoles **9b** and **9c**, respectively (Scheme 4), plus the side product **12** and triphenylphosphane oxide.



Scheme 4.

Analogously, the methoxycarbonyl-substituted ylide **5** reacts under photochemical conditions with acetonitrile, propionitrile, and benzonitrile to afford the oxazoles **10a**, **10b**, and **10c**, respectively (Scheme 4). Furthermore we found that the replacement of the ethoxycarbonyl group with the benzoyl group in the starting ylide **6** leads to a remarkable increase in the reactivity. Indeed, the photochemical reac-



Scheme 5.

tions of the ylide **6** with the three nitriles afforded the oxazoles **11a**, **11b**, and **11c** in yields of 60%, 60%, and 35%, respectively. Moreover the ylide **6** also reacted with 4-cyanopyridine (**15**) and diethylcyanamide (**16**) to yield the oxazoles **17** and **18**, respectively (Scheme 5).

Conclusions

We have found a novel class of photochemical reactions between mixed phosphonium-iodonium ylides and nitriles to yield polyfunctional 2,4,5-trisubstituted oxazoles.

Experimental Section

General: The ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on a Bruker Avance 400 instrument operating at 400 MHz in $CDCl_3$ or CD_3CN with Me_4Si as the internal standard. The IR spectra were measured on a UR-20 instrument in CCl_4. The elemental analysis was carried out on a Vario-II CHN analyzer. The mass spectra were obtained on a Finnigan Mat Incos50 quadrupole mass spectrometer (EI, 70 eV, direct inlet) and an Agilent LC/MSD 1100 SL instrument with electrospray ionization at atmospheric pressure (AP-ESI) in the positive ion detection mode (an ion trap as a mass analyzer). Recording conditions: temperature of the drying gas (nitrogen) 300 °C, flow rate 12 L min^{-1}, power supply voltage 5000 V, capillary outlet voltage 150 V, acetonitrile as solvent. The reaction progress and the purity after chromatographic separation were monitored by TLC on Silufol plates. Chromatographic separation was carried out on columns with Merck 60 (0.063–0.200 mm) silica gel.

General Procedure for the Reactions between Ylides 4–6 and Nitriles: An ylide **4**–**6** (0.2 g) was added to a nitrile (2–4 mL). In the case of 4-cyanopyridine we used dichloromethane as solvent. The reaction mixtures were irradiated under argon in a quartz flask with a mercury light (254 nm) source. The course of the reaction was monitored by TLC. After the end of the reaction the mixtures with acetonitrile or dichloromethane as solvents were concentrated in vacuo and the residue was dissolved in a minimum of CH_2Cl_2 and chromatographed on silica gel. The reaction mixtures with other nitriles were chromatographed on silica gel without concentration. To elute the nitriles and admixtures, benzene and CH_2Cl_2 were used; triphenylphosphane oxide, the corresponding oxazole, and the phosphonium salt (**12**–**14**) were eluted with CH_2Cl_2/MeOH mixtures in a ratio from 100:1 to 20:1 (all oxazoles were eluted with a CH_2Cl_2/MeOH mixture in a 100:1 ratio).

9a: Yields of isolated products: **9a** (50 mg, 35%), **12** (50 mg, 35%), and triphenylphosphane oxide (25 mg, 30%). **9a**: ^{1}H NMR ($CDCl_3$): δ = 0.99 (t, 3 H, CH_3), 2.49 (s, 3 H, CH_3), 4.32 (q, 2 H, CH_2), 7.65–7.80 (m, 15 H, arom.) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.15 (s, CH_3), 14.22 (s, CH_3), 70.63 (s, OCH_2), 118.21 (d, $^1J_{C,P}$ = 95.3 Hz, C_{ipso} arom.), 130.19 (d, $^3J_{C,P}$ = 13.9 Hz, C_m arom.), 134.19 (d, $^2J_{C,P}$ = 11.0 Hz, C_o arom.), 135.21 (s, C_p arom.), 155.47 (s, C–O), 167.01 (c, C–CH_3) ppm. ^{31}P NMR ($CDCl_3$): δ = 8.64 ppm. IR: $\tilde{\nu}$ = 1590, 1630 (cycle), 1730 (C=O) cm^{-1}. MS: *m*/*z* = 388 $[M - BF_4]^+$.

9b: Yields of isolated products: **9b** (30 mg, 20%), **12** (55 mg, 40%), triphenylphosphane oxide (25 mg, 30%). **9b**: ^{1}H NMR ($CDCl_3$): δ = 1.01 (t, 3 H, CH_3), 1.34 (t, 3 H, CH_3), 2.82 (q, 2 H, CH_2), 4.34 (q, 2 H, CH_2), 7.68–7.82 (m, 15 H, arom.) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.44 (s, CH_3), 14.22 (s, CH_3), 21.75 (s, CH_2), 70.56 (s, OCH_2), 118.20 (d, $^1J_{C,P}$ = 94.4 Hz, C_{ipso} arom.), 130.20 (d, $^3J_{C,P}$ = 13.2 Hz, C_m arom.), 134.17 (d, $^2J_{C,P}$ = 11.0 Hz, C_o arom.), 135.22 (d, $^4J_{C,P}$ = 2.2 Hz, C_p arom.), 159.44 (d, $^3J_{C,P}$ = 19.0 Hz, C=N), 169.12 (s, C–O) ppm. ^{31}P NMR ($CDCl_3$): δ = 8.56 ppm. IR: $\tilde{\nu}$ = 980–1120 (BF_4) 1230–1630 (cycle) cm^{-1}. MS: *m*/*z* = 402 $[M - BF_4]^+$.

9c: Yields of isolated products: **9c** (25 mg, 15%), **12** (80 mg, 60%), triphenylphosphane oxide (20 mg, 25%). **9c**: ^{1}H NMR ($CDCl_3$): δ = 1.11 (t, 3 H, CH_3), 4.51 (q, 2 H, CH_2), 7.48–7.98 (m, 20 H, arom.) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.28 (s, CH_3), 71.17 (s, OCH_2), 117.90 (d, $^1J_{C,P}$ = 95.2 Hz, C_{ipso} arom.), 126.34 (s, C_o arom.), 129.04 (s, C_m arom.), 130.32 (d, $^3J_{C,P}$ = 13.1 Hz, C_m arom.), 131.41 (s, C_p arom.), 132.96 (s, C_{ipso} arom.), 134.24 (d, $^2J_{C,P}$ = 11.0 Hz, C_o arom.), 135.44 (s, C_p arom.), 155.13 (d, $^3J_{C,P}$ = 19.8 Hz, C=N), 166.83 (d, $^2J_{C,P}$ = 27.1 Hz, C–O) ppm. ^{31}P NMR ($CDCl_3$): δ = 8.81 ppm. IR: $\tilde{\nu}$ = 1260–1630 (cycle), 1000–1200 (BF_4) cm^{-1}. $C_{29}H_{25}BF_4NO_2P$ (537.30): calcd. C 64.80, H 4.66, N 2.61; found C 64.78, H 4.81, N 2.68.

10a: Yields of isolated products: **10a** (35 mg, 25%), **13** (55 mg, 49%), triphenylphosphane oxide (25 mg, 30%). **10a**: ^{1}H NMR ($CDCl_3$): δ = 2.50 (s, 3 H, CH_3), 3.98 (s, 3 H, OCH_3), 7.67–7.83 (m, 15 H, arom.) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.14 (s, CH_3), 60.61 (s, OCH_3), 118.16 (d, $^1J_{C,P}$ = 95.1 Hz, C_{ipso} arom.), 130.18 (d, $^3J_{C,P}$ = 13.9 Hz, C_m arom.), 134.18 (d, $^2J_{C,P}$ = 11.0 Hz, C_o arom.), 135.20 (d, $^4J_{C,P}$ = 2.2 Hz, C_p arom.), 156.01 (s, C=N), 167.58 (d, $^2J_{C,P}$ = 26.3 Hz, C–O) ppm. ^{31}P NMR ($CDCl_3$): δ = 8.88 ppm. IR: $\tilde{\nu}$ = 1280–1680 (cycle), 1000–1200 (BF_4) cm^{-1}. $C_{23}H_{21}BF_4NO_2P$ (461.20): calcd. C 59.87, H 4.56, N 3.04; found C 60.24, H 4.75, N 2.91.

10b: Yields of isolated products: **10b** (20 mg, 15%), **13** (60 mg, 45%), triphenylphosphane oxide (35 mg, 40%). **10b**: ^{1}H NMR ($CDCl_3$): δ = 1.34 (t, *J* = 7.6 Hz, 3 H, CH_3), 2.83 (q, *J* = 7.5 Hz, 2 H, OCH_2), 3.06 (s, 3 H, OCH_3), 7.65–7.84 (m, 15 H, arom.) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.43 (s, CH_3), 21.76 (s, CH_2), 60.55 (s, OCH_3), 118.12 (d, $^1J_{C,P}$ = 94.4 Hz, C_{ipso} arom.), 130.20 (d, $^3J_{C,P}$ = 13.1 Hz, C_m arom.), 134.17 (d, $^2J_{C,P}$ = 11.0 Hz, C_o arom.), 135.25 (s, C_p arom.), 159.40 (s, $^3J_{C,P}$ = 18.3 Hz, C–O), 167.41 (d, $^2J_{C,P}$ = 27.0 Hz, C–O) ppm. ^{31}P NMR ($CDCl_3$): δ = 8.92 ppm. IR: $\tilde{\nu}$ = 1280, 1680 (cycle), 1000–1200 (BF_4) cm^{-1}. MS: *m*/*z*: 388 $[M - BF_4]^+$.

10c: Yields of isolated products: **10c** (20 mg, 13%), **13** (60 mg, 45%), triphenylphosphane oxide (35 mg, 40%). **10c**: ^{1}H NMR ($CDCl_3$): δ = 4.04 (s, 3 H, OCH_3), 7.58–8.03 (m, 20 H, arom.) ppm. ^{13}C NMR (CD_3CN): δ = 60.43 (s, OCH_3), 118.06 (d, $^1J_{C,P}$ = 94.4 Hz, C_{ipso} arom.), 125.94 (s, C_o arom.), 129.25 (s, C_m arom.), 130.12 (d, $^3J_{C,P}$ = 13.2 Hz, C_m arom.), 131.39 (s, C_p arom.), 134.41 (d, $^2J_{C,P}$ = 11.0 Hz, C_o arom.), 135.38 (s, *J* = 3.0 Hz, C_p arom.), 154.58 (d, $^3J_{C,P}$ = 19.0 Hz, C=N), 167.38 (d, $^2J_{C,P}$ = 26.3 Hz, C–O) ppm. ^{31}P NMR ($CDCl_3$): δ = 9.21 ppm. IR: $\tilde{\nu}$ = 1000–1140 (BF_4), 1290–1620 (cycle) cm^{-1}. $C_{28}H_{23}BF_4NO_2P$ (523.27): calcd. C 64.24, H 4.40, N 2.68; found C 63.96, H 4.52, N 2.60.

11a: Yields of isolated products: **11a** (90 mg, 60%), **14** (60 mg, 30%), triphenylphosphane oxide (8 mg, 10%). **11a**: ^{1}H NMR ($CDCl_3$): δ = 2.62 (s, 3 H, CH_3), 7.59–7.87 (m, 20 H, arom.) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.06 (s, CH_3), 116.89 (d, $^1J_{C,P}$ = 93.7 Hz, C_{ipso} arom.), 128.50 (s, C_m arom.), 128.66 (s, C_o arom.), 130.42 (d, $^3J_{C,P}$ = 13.2 Hz, C_m arom.), 130.87 (s, C_p arom.), 134.46 (d, $^2J_{C,P}$ = 10.2 Hz, C_o arom.), 135.66 (s, C_p arom.), 163.88 (d, ^2J = 30.0 Hz, C–O), 164.25 (d, ^3J = 19.0 Hz, C=N) ppm. ^{31}P NMR ($CDCl_3$): δ = 11.84 ppm. IR: $\tilde{\nu}$ = 980–1120 (BF_4), 1180, 1630 (cycle) cm^{-1}. $C_{28}H_{23}BF_4NOP$ (507.28): calcd. C 66.27, H 4.54, N 2.76; found C 66.24, H 4.25, N 2.58.

11b: Yields of isolated products: **11b** (95 mg, 60%), **14** (40 mg, 30%), triphenylphosphane oxide (8 mg, 10%). **11b**: ^{1}H NMR ($CDCl_3$): δ = 1.41 (t, J = 7.3 Hz, 3 H, CH_3), 2.98 (q, J = 7.3 Hz, 2 H, CH_2), 7.05 (s, 4 H, arom.), 7.22 (s, 1 H, arom.), 7.59–7.87 (m, 15 H, arom.) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.60 (s, CH_3), 21.64 (s, CH_2), 114.28 (d, ^1J = 135.4 Hz, $C_{ox.}$–P), 116.83 (d, $^1J_{C,P}$ = 93.7 Hz, C_{ipso} arom.), 124.93 (s, C_{ipso} arom.), 128.48 (s, C_m arom.), 128.58 (s, C_o arom.), 130.40 (d, $^3J_{C,P}$ = 13.9 Hz, C_m arom.), 130.85 (s, C_p arom.), 134.40 (d, $^2J_{C,P}$ = 10.9 Hz, C_o arom.), 135.69 (s, C_p arom.), 163.64 (d, J = 29.2 Hz, C–O), 168.33 (d, J = 19.8 Hz, C=N) ppm. ^{31}P NMR ($CDCl_3$): δ = 11.81 ppm. IR: $\tilde{\nu}$ = 1000–1120 (BF_4) 1180, 1620 (cycle) cm^{-1}. $C_{29}H_{25}BF_4NOP$ (521.22): calcd. C 66.79, H 4.80, N 2.69; found C 66.98, H 4.96, N 2.74.

11c: Yields of isolated products: **11c** (60 mg, 35%), **14** (40 mg, 30%), triphenylphosphane oxide (30 mg, 35%). **11c**: ^{1}H NMR ($CDCl_3$): δ = 7.14 (s, 4 H, arom.), 7.29 (s, 2 H, arom.), 7.59–7.87 (m, 15 H, arom.), 8.09 (d, 4 H, arom.) ppm. ^{13}C NMR ($CDCl_3$): δ = 116.19 (d, ^1J = 133.9 Hz, C_{ox}–P), 116.59 (d, $^1J_{C,P}$ = 94.1 Hz, C_{ipso} arom.), 124.66 (s, C_{ipso} arom.), 125.09 (s, C_{ipso} arom.), 127.22 (s, C_o arom.), 128.59 (s, C_m arom.), 128.72 (s, C_m arom.), 129.23 (s, C_o arom.), 130.55 (d, $^3J_{C,P}$ = 13.1 Hz, C_m arom.), 131.26 (s, C_p arom.), 132.35 (s, C_p arom.), 134.48 (d, $^2J_{C,P}$ = 10.9 Hz, C_o arom.), 135.91 (s, C_p arom.), 163.37 (d, ^2J = 28.6 Hz, C–O), 163.77 (d, ^3J = 19.8 Hz, C=N) ppm. ^{31}P NMR ($CDCl_3$): δ = 12.24 ppm. IR: $\tilde{\nu}$ = 1280–1660 (cycle), 1000–1200 (BF_4) cm^{-1}. MS, m/z: 482 [M – BF_4]$^+$.

17: Yields of isolated products: **17** (40 mg, 25%), **14** (70 mg, 55%), triphenylphosphane oxide (15 mg, 20%). **17**: ^{1}H NMR ($CDCl_3$): δ = 7.10–7.86 (m, 22 H, arom.), 8.46 (d, 2 H, arom.) ppm. ^{13}C NMR ($CDCl_3$): δ = 120.93 (d, $^1J_{C,P}$ = 92.94 Hz, C_{ipso} arom.), 126.10 (s, C_p arom.), 127.10 (s, C_o Py arom.), 128.87 (s, C_m arom.), 128.79 (d, $^3J_{C,P}$ = 13.2 Hz, C_m arom.), 130.11 (s, C_o arom.), 130.41 (s, C_{ipso} arom.), 133.20 (d, $^2J_{C,P}$ = 11.0 Hz, C_o arom.), 133.91 (d, $^4J_{C,P}$ = 1.5.0 Hz, C_p arom.), 140.44 (s, C_{ipso} Py arom.), 151.99 (s, C_m Py arom.), 157.26 (s, C–O), 159.02 (s, C=N) ppm. ^{31}P NMR ($CDCl_3$): δ = 16.80 ppm. IR: $\tilde{\nu}$ = 1280–1620 (cycle), 1000–1150 (BF_4) cm^{-1}. MS, m/z: 483 [M – BF_4]$^+$.

18: Yields of isolated products: **18** (50 mg, 30%), **14** (40 mg, 30%), triphenylphosphane oxide (30 mg, 35%). **18**: ^{1}H NMR ($CDCl_3$): δ = 1.26 (t, J = 7.0 Hz, 6 H, CH_3), 3.53 (q, J = 7.1 Hz, 4 H, CH_2), 6.95 (d, 2 H, arom.), 7.03 (t, 2 H, arom.), 7.18 (t, 1 H, arom.), 7.60–7.79 (m, 15 H, arom.) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.31 (s, CH_3), 43.42 (s, CH_2), 114.26 (d, ^1J = 133.9 Hz, C_{ox}–P), 117.18 (d, $^1J_{C,P}$ = 93.7 Hz, C_{ipso} arom.), 125.45 (s, C_{ipso} arom.), 128.13 (s, C_m arom.), 128.39 (s, C_o arom.), 130.08 (s, C_p arom.), 130.24 (d, $^3J_{C,P}$ = 13.2 Hz, C_m arom.), 134.45 (d, $^2J_{C,P}$ = 11.0 Hz, C_o arom.), 135.58 (s, C_p arom.), 161.71 (d, ^2J = 17.5 Hz, C=N), 168.10 (s, C–O) ppm. ^{31}P NMR ($CDCl_3$): δ = 11.59 ppm. IR: $\tilde{\nu}$ = 1000–1140 (BF_4) 1290–1620 (cycle) cm^{-1}. MS: m/z: 477 [M – BF_4]$^+$.

X-ray Diffraction Analysis of 9a: The reflections were collected with a Nonius CAD4 diffractometer (Mo-K_α radiation, graphite monochromator at 293 K). Cell parameters were determined from a set of 23 reflections. Absorption corrections by crystal shape were applied to the set of experimental data. The structure was solved by direct methods (SIR2002 program package);[13] other non-hydrogen atoms were found by a number of Fourier and difference Fourier synthesis and were then refined in successive isotropic and anisotropic (except atoms of the BF_4 group) approximations by use of the JANA2000 program package.[14] Hydrogen atoms were treated by appropriate riding methods. Details of the crystallographic data and the refinement procedures are given in Table 1.

Table 1. Crystal data and details of the refinement procedure for **9a**.

Empirical formula	$C_{24}H_{23}BF_4NO_2P$
Formula weight	475.23
Crystal form	plate
Crystal size [mm]	0.32 × 0.81 × 0.04
Crystal system	monoclinic
Space group	$P2_1/a$
Unit cell dimensions [Å]	a = 12.711(4) b = 14.574(2) c = 13.031(3) β = 103.30(2)
V [Å^3]	2349.3 (10)
Z	4
$D_{calcd.}$ [g cm^{-3}]	1.343
Radiation, λ [Å]	Mo-K_α, 0.71069
Temperature [K]	293
Data collection method	ω
Absorption correction	analytical (crystal shape)
No. of measured reflection	5793
No. of independent reflection	2599
No. of observed reflection [$I > 3\sigma(I)$]	2060
θ limits [°]	2–26
Range of h, k, l	$0 \le h \le 15$, $-2 \le k \le 17$ $-16 \le l \le 15$
R_{int}	0.025
R/R_w [$I > 3\sigma(I)$]	0.074/0.105
Goodness of fit	1.60
No. of refined parameters	339
Weighting scheme	$w = [\sigma^2(F) + (0.055F)^2]^{-1}$
$\Delta\delta$ [e Å^{-3}] max./min.	+0.39/–0.55

CCDC-705116 (for **9a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.cam.ac.uk/data_request.cif.

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