# A Wittig Reaction with 2-Furyl Substituents at the Phosphorus Atom: Improved (*Z*) Selectivity and Isolation of a Stable Oxaphosphetane Intermediate

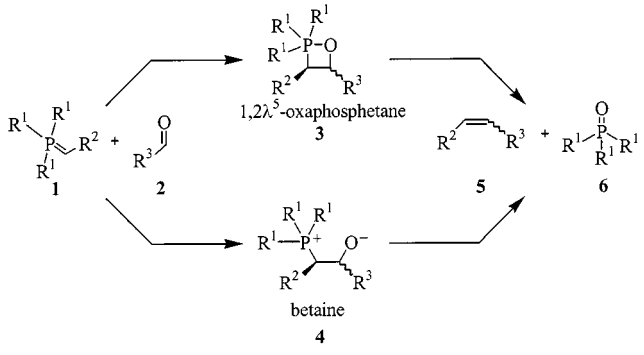
**Marco Appel,[a] Steffen Blaurock,[a] and Stefan Berger*[a]**

**Keywords:** NMR spectroscopy / Oxaphosphetanes / Stereoselectivity / Wittig reactions

Wittig reactions with ylides bearing one, two or three 2-furyl groups directly bound to the phosphorus atom have been studied. Greatly improved (*Z*)-alkene selectivities of up to 98:2 could be observed if 2-furyl groups were present. Monitoring of the reactions by NMR spectroscopy revealed only oxaphosphetane intermediates, which became more stable with increasing number of 2-furyl substituents bound to the phosphorus atom. Oxaphosphetane **10d**, with three furyl groups, was successfully isolated, and the results of a crystal structure analysis are presented.


## Introduction

The Wittig reaction is one of the most powerful methods for the preparation of carbon−carbon double bonds and is used as a key step in many natural product syntheses[1] as well as in industrial processes.[2] The main advantages of this reaction are the regioselective formation of the double bond at the position of the former carbonyl group and the potential to control the stereoselectivity by application of particular reaction conditions.[3] Because of its synthetic importance, the mechanism of the Wittig reaction was long hotly contested. Earlier it was believed that the main intermediates in typical Wittig reactions were betaines **4**[4] (Scheme 1).




Scheme 1.

In 1973, however, Vedejs et al. were able to prove that only 1,2λ$^5$-oxaphosphetanes **3** could be detected by NMR spectroscopy during typical Wittig reactions.[5] These intermediates are normally unstable and decompose readily upon warming to room temperature, into the desired alkene **5** and phosphane oxide **6**. Nevertheless, several stabilized, isolable oxaphosphetanes have been reported in the literature, along with their X-ray structures.[6−11]

We have been studying the influence of heteroaromatic substituents on Wittig reactions since the reported failure of a Wittig reaction between triphenyl(methylene)phosphorane and 2,2′-dipyridyl ketone in the presence of lithium salts.[12] This was due to the formation of stable betaines, which could be observed in the presence of lithium ions, when two or more 2-pyridyl substituents were bound either to the carbonyl compound,[13] or to the phosphorus atom.[14] Interestingly, improved (*Z*)-alkene selectivities could be observed in the latter case.

As objects for further systematic investigations, 2-furyl substituents were selected, since we reasoned that the electronegative oxygen atom should be better suited for complexing lithium ions, and this should mean greater betaine stability than in the pyridyl case. Two studies involving 2-furyl systems in Wittig reactions have been published,[15,16] but only the work of Schlosser et al. dealt with influences of 2-furyl groups on the stereoselectivity of the reaction, and in neither case was information about reaction intermediates given.

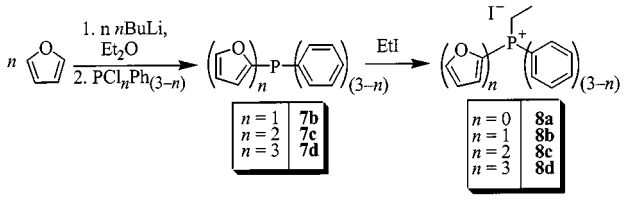
Here we wish to report our observations of greatly improved (*Z*)-alkene selectivities when 2-furyl groups were bound to the phosphorus atom. Surprisingly, no betaines could be detected, but the observed 1,2λ$^5$-oxaphosphetanes were thermally exceptionally stable, permitting their isolation and the recording of an X-ray crystallographic structure.

[a] Institut für Analytische Chemie, Fakultät für Chemie und Mineralogie, Universität Leipzig,
Linnéstraße 3, 04103 Leipzig, Germany
Fax: (internat.) + 49-(0)341/97-11833
E-mail: stberger@rz.uni-leipzig.de

## Results and Discussion

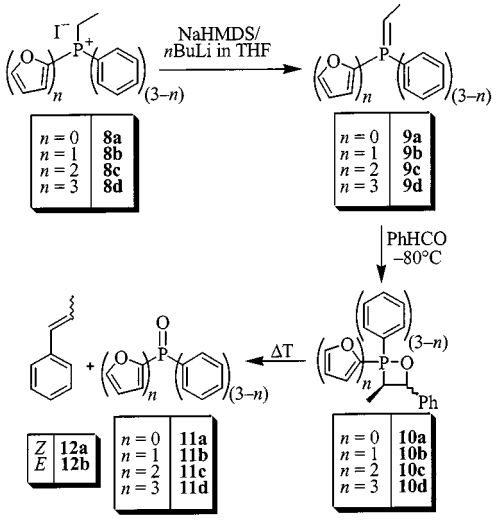
### Synthetic Observations

The Wittig reaction chosen for our studies was that between benzaldehyde and ethylphosphonium salts, deprotonated either with NaHMDS or with *n*-butyllithium. The required phosphonium salts bearing 2-furyl groups are very easily accessible from cheap chemicals. The corresponding phosphanes with one, two or all three phenyl groups replaced by 2-furyl substituents (**7a**, **7b** and **7c**) were prepared by known procedures.[15] Quaternization with ethyl iodide[17] provided the investigated phosphonium salts **8b**, **8c** and **8d** (Scheme 2).




Scheme 2. Synthesis of phosphonium iodides

All Wittig reactions were carried out in THF as solvent, and benzaldehyde was added to the ylide[18,19] solution at −80 °C (Scheme 3).




Scheme 3. Investigated Wittig reactions

The Wittig reaction between ethylidenetriphenylphosphorane **9a** and benzaldehyde is known in the literature, and results have been published by different authors.[5,14,20−22] In our work with phosphonium salts bearing 2-furyl groups, only poor yields were initially obtained, when standard Wittig procedures were applied.[22] We found, however, that the yield could be increased to the levels presented in Table 1 when the mixtures were heated to 70 °C for several hours prior to workup. Our results are shown in Table 1.

Table 1. Yield and stereochemical outcome of Wittig reactions with ethyl(furyl)phosphonium salts and benzaldehyde, with either NaHMDS or *n*BuLi as base

| Compound | *n*BuLi | | NaHMDS | |
|---|---|---|---|---|
| | (*Z*)/(*E*)[a] | Yield[b] | (*Z*)/(*E*) | Yield |
| $EtPh_3P^+ I^-$ (**8a**) | 60:40 | 76% | 70:30 | 78% |
| $EtFuPh_2P^+ I^-$ (**8b**) | 81:19 | 76% | 94:6 | 76% |
| $EtFu_2PhP^+ I^-$ (**8c**) | 89:11 | 46% | 96:4 | 73% |
| $EtFu_3P^+ I^-$ (**8d**) | 82:18 | 35% | 98:2 | 61% |

[a] (*Z*)/(*E*) ratios were determined on isolated product by NMR spectroscopy and GC. [b] All yields were determined on isolated products.

Comparison of these results with previously published data shows that, for the standard reaction with three phenyl substituents and with NaHMDS as base, both yield and (*Z*)/(*E*) ratio were lower than those reported in the literature. This can probably be explained by the influence of sodium iodide. Iodide is known to affect both yield and stereochemical outcome of Wittig reactions,[23,24] especially in the presence of sodium ions.

However, a significant effect of the 2-furyl groups on the stereoselectivity can be seen in Table 1. One single 2-furyl substituent at the phosphorus atom increased the (*Z*) selectivity from 70:30 to 94:6.[25] With three 2-furyl groups, the (*Z*) selectivity reached the level of 98:2. Schlosser et al. have published a (*Z*) selectivity of 96:4 obtained with the phosphonium salt **8d**[16] and the bromide salt with sodium amide as base; yields were not reported in that case. We observed only a slight decrease in overall yield, in comparison to that obtained with the standard phenyl ligands. Addition of the aldehyde to the ylide **9d** at room temperature resulted in a (*Z*)/(*E*) ratio of 9:1. It has been reported in the literature that the temperature at which the aldehyde is added to the ylide is very important for optimum (*Z*)-alkene selectivities,[22] since the selectivity has its origin in kinetic reaction control.

In cases in which *n*-butyllithium was used as base, the stereoselective effect of the 2-furyl groups was less pronounced and the yield decreased remarkably. However, in contrast to the reactions with pyridyl systems,[14] there were always isolable amounts of product present, indicating the absence of stable betaines.

It may thus be noted that 2-furyl groups are able to increase the stereoselectivity of Wittig reactions greatly, and are also somehow able to mitigate the negative effects of iodide anions. Experimental results indicated the absence of betaines, but the presence of significantly more stable reaction intermediates, as the reaction mixtures had to be heated in order to obtain good yields.

### NMR-Spectroscopic Investigations

All reactions were monitored by low-temperature NMR spectroscopy in order to identify and characterise the reac-

tion intermediates and to gain some information about the origin of the greatly improved (*Z*) selectivity.

**Characterization of Ylides**

Information about the preferred conformations of the ylides could be especially important, since it is now widely accepted that the stereochemistry of Wittig reactions is determined in the oxaphosphetane-forming step. This key step is believed to resemble a [2+2] cycloaddition between the ylide and the carbonyl compound. In the case of reactive ylides,[26] as present in the Wittig reactions discussed here, the transition state of this reaction is early. The observed alkene selectivities are the consequence of energy differences in the transition states on the routes to either the (*Z*)- or the (*E*)-oxaphosphetane.[27,28] The (*Z*)-oxaphosphetane should therefore be formed preferably under kinetic control conditions. Unfortunately, this key step of any Wittig reaction is too fast to be observed by NMR methods; not even investigations with rapid injection techniques provided any information.[29] Our aim was to characterise the ylides carefully and to gain information about the preferred conformations of these molecules, which could help in explaining the improved (*Z*)-alkene selectivities.

The ylides were prepared in small flasks and transferred into NMR tubes, with careful exclusion of air and moisture. Standard $^{1}H$ and $^{31}P$ NMR spectra, together with 2D NOESY and ROESY spectra, were recorded at different temperatures to identify the favoured conformation of the ylides. Figure 1 presents the 2D-NOESY spectrum of ylide **9b**.

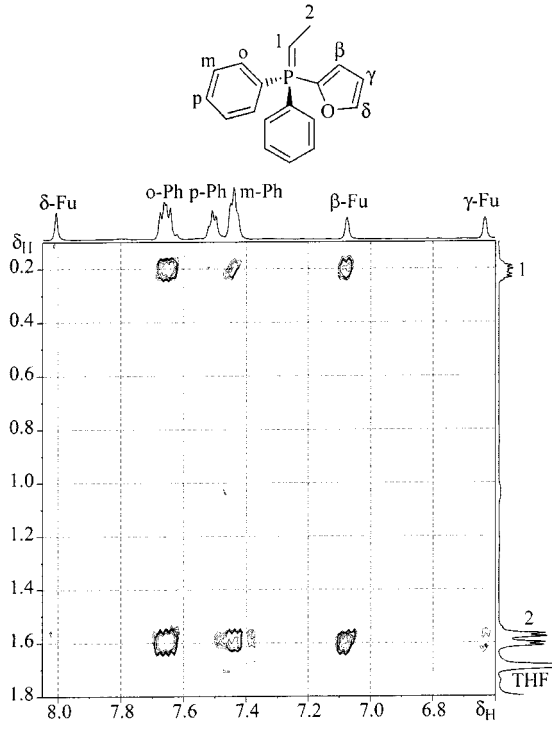



Figure 1. Detail of the 2D-NOESY spectrum of ylide **9b** at 600 MHz and −100 °C

Strong NOE contacts could be observed between proton 1 at the carbanionic centre and the β-furyl and *ortho*- and *meta*-phenyl protons. The methyl group protons 2 had the same contacts. These findings, together with the sharp signals of the furyl and phenyl protons even at −100 °C, indicated fast rotation of the groups attached to the phosphorus atom. These results are at variance with our earlier proposal − which would have explained the favoured formation of (*Z*)-oxaphosphetane in the presence of pyridyl groups − of a rigid metal chelate complex of the ylides with cations in solution.[14]

Since metal chelation and concomitant hindered rotation of the furyl rings is not supported by the results of the NMR spectra, the observed change in stereoselectivity may have its cause in the electronic interactions of the furyl ring attached to the ylide. A detailed theoretical study of such effects, however, is at present not available.

**Characterization of Oxaphosphetanes**

After addition of benzaldehyde to the ylide solutions, only 1,2$\lambda^5$-oxaphosphetane intermediates could be observed in $^{31}P$ chemical shift regions typical for pentavalent phosphorus species (from $\delta = -75$ to $\delta = -100$). No hint of the presence of betaine intermediates could be detected, in clear contrast to the case of 2-pyridyl rings.[14] It appears that the furyl oxygen atom is not able to form metal chelate complexes with lithium ions, which stabilise the betaines.

The observed $^{1}H$ NMR spectra of the oxaphosphetanes **10b**, **10c** and **10d** were quite complex. The phosphorus atoms in compounds **10b** and **10c** are chiral, and the 2-furyl or phenyl groups are therefore diastereotopic. Furthermore, the β-furyl proton signals split into complex patterns at temperatures below −50 °C, as rotation around the P−C bond becomes slower. In the 2D-NOESY and ROESY spectra, NOE contacts mainly from protons at ring carbon atoms to the β-furyl and *ortho*-phenyl protons can be seen. This is in agreement with typical oxaphosphetane structures.

In the $^{31}P$ NMR spectra, two signals for the (*Z*)- and (*E*)-oxaphosphetane were always present, and the ratios remained the same on heating the mixtures. Exactly the same ratios could be observed in isolated products after workup. No stereochemical drift[30] is therefore present, and so − for the furyl systems − the stereochemistry is indeed decided in the oxaphosphetane-forming step. However, during warming of the oxaphosphetane solutions we made an interesting discovery. The decomposition of the oxaphosphetanes required higher temperatures with increasing number of 2-furyl groups present at the phosphorus atom. Standard phenyl group bearing oxaphosphetanes, such as **10a**, decompose readily on warming to room temperature.[30] In contrast, oxaphosphetane **10d**, with three 2-furyl groups, showed a half life of 1 h at 50 °C. This significant stabilization can be explained in terms of the electronic effects of the furyl systems. Table 2 presents the $^{31}P$ NMR chemical shifts of all observed phosphorus species during Wittig reactions.

Table 2. $^{31}P$ NMR chemical shifts of all observed phosphorus species

| Number $n$ of furyl rings | $\delta$[a][b] of phosphane | $\delta$[b] of phosphonium salt | $\delta$[c] of ylide | $\delta$[c] [d] of oxaphosphetane | $\delta$[c] of phosphanoxide |
|---|---|---|---|---|---|
| $n = 1$ | **7b**: −26.3 | **8b**: 16.3 | **9b**: 2.6 | **10b**: −73.7 (−73.8) | **11b**: 16.4 |
| $n = 2$ | **7c**: −50.3 | **8c**: 4.4 | **9c**: −12.1 | **10c**: −87.0 (−88.9) | **11c**: 2.3 |
| $n = 3$ | **7d**: −76.8 | **8d**: −9.6 | **9d**: −30.9 | **10d**: −101.4 (−102.0) | **11d**: −12.9 |

[a] All chemical shifts were measured with 85% phosphoric acid as external standard. [b] Solvent used for $^{31}P$ NMR: $CDCl_3$. [c] Solvent used for $^{31}P$ NMR: [$D_8$]THF. [d] $^{31}P$ NMR chemical shifts for (*Z*)-oxaphosphetane, the shift value for the (*E*)-oxaphosphetane is given in brackets.

The $^{31}P$ NMR chemical shifts are shifted to lower frequency with increasing number of 2-furyl groups present at the phosphorus centre. Comparison of the measured shifts with those previously reported in systematic studies of ligand effects on phosphorus chemical shifts[31] suggests the conclusion that 2-furyl groups have electron-withdrawing properties. This is in agreement with a recently published review[32] on the use of the tris(2-furyl)phosphane ligand in Stille-type reactions. Since all but one of the stable oxaphosphetanes so far reported featured several fluorine-containing groups at the phosphorus atom or at ring carbon atoms, it is experimentally established that electron-withdrawing groups are able to stabilize oxaphosphetanes and other semistable intermediates.

### Isolation and Crystal Structure Analysis of Oxaphosphetane 10d

Encouraged by the observation of increased thermal stability in oxaphosphetanes bearing 2-furyl groups, we successfully isolated oxaphosphetane **10d** by evaporation of the solvent and recrystallisation from chloroform. The isolated crystals were suitable for crystal structure analysis, and the obtained structure is presented in Figure 2.

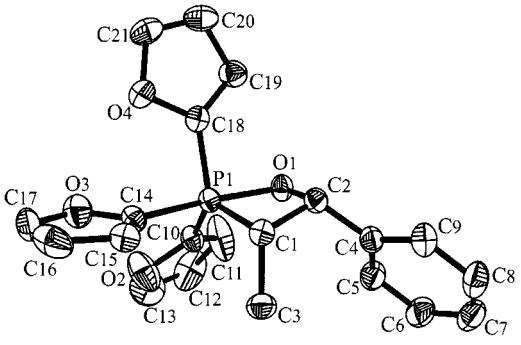



Figure 2. ORTEP drawing of crystal structure of oxaphosphetane **10d**; selected bond lengths [Å]: P1−C1 1.84(1), C1−C2 1.55(1), C2−O1 1.43(1), P1−O1 1.78(1)

The phosphorus atom is at the centre of a slightly disturbed trigonal bipyramid, the angle between the two apical positions and the phosphorus atom (C14−P1−O1) being 172.1°. The four-membered oxaphosphetane ring is in an apical equatorial position and is puckered, as the plane containing atoms C1, P1 and O1 and the plane containing the atoms O1, C1 and C2 form a dihedral angle of 18.2°. This dihedral angle is quite large in comparison with previously published results in which dihedral angles between 0.6° and 9.7° were reported.[6−11] The equatorial furyl substituents are almost orthogonal to the trigonal plane, with interplane angles of 75.6° and 86.4°, respectively. The P−O bond length is 1.78 Å, which is among the shortest in the range of reported P−O bond lengths in oxaphosphetanes (from 1.73 to 2.01 Å).

It may be noted that the main features of the oxaphosphetane **10d** structure, such as the disturbed trigonal-bipyramidal coordination of the phosphorus atom, are in agreement with previously published results, mainly from the groups of Ramirez and Okazaki.[6−9] However, it should be pointed out that all previously published oxaphosphetane structures contained fluorine-bearing or bicyclic phospholetype ligands either at the phosphorus position or at the 4 position in the oxaphosphetane ring. Decomposition temperatures of these "artificial" oxaphosphetanes were higher by up to 200 °C. We were able to obtain a stable oxaphosphetane simply by exchanging the standard phenyl groups for 2-furyl systems, and so isolated a Wittig reaction intermediate that might be closer to standard organic practice than fluorine-containing oxaphosphetanes.

## Conclusion

In this work we have been able to show that 2-furyl substituents at the phosphorus atom give rise to two main effects in Wittig reactions with reactive ylides: firstly, greatly improved (*Z*)-alkene selectivity in the reaction, and secondly, significant increases in the thermal stability of the oxaphosphetane intermediates. The origin of the improved (*Z*)-selectivity observed with the presence of heteroaromatic systems bound directly to the phosphorus atom remains as yet unclear. Electron-withdrawing effects of these groups are influencing the transition state in such a way that the (*Z*)-oxaphosphetane is formed preferably. The stabilization of intermediates can also be attributed to the electron-withdrawing properties of the 2-furyl substituents. As a result of this significant stabilization, we were able to isolate an $1,2\lambda^5$-oxaphosphetane bearing three 2-furyl substituents at the phosphorus atom. The recorded X-ray crystal structure revealed that the phosphorus atom is at the centre of a disturbed trigonal bipyramid and that the four-membered ring is puckered.

Further studies to clarify the origin of the increased (*Z*)-alkene selectivities are currently underway.

## Experimental Section

**General Remarks:** All reactions were carried out with careful exclusion of moisture and air. The THF used was dried with sodium/benzophenone and freshly distilled prior to use. The benzaldehyde was also distilled. All routine NMR spectra were recorded with a Bruker DRX 400 spectrometer in $CDCl_3$, with TMS as internal shift reference. The 2D-NOESY spectrum of ylide **9b** was recorded with a Bruker DRX 600 in [$D_8$]THF, shifts being referred to traces of undeuterated solvent. $^{31}P$ NMR chemical shifts were always referred to external 85% phosphoric acid. The IR spectrum was recorded with a Perkin−Elmer FT-IR spectrometer 1725X in KBr. The high-resolution mass spectra were recorded with a Bruker 7T APEX II FT-ICR mass spectrometer using ESI ionisation.

**Synthesis:** The 2-furyl(phenyl)phosphanes **7b**, **7c** and **7d** were prepared by the method described by Allen et al.[15] The corresponding phosphonium salts **8b**, **8c** and **8d** were obtained by a method described by Schmidbaur et al.[17] and recrystallized from ethanol.

**Phosphonium Salt 8a:** Yield 95%; m.p. 169−171 °C (ref.[33] 169−173 °C). $^{31}P$ NMR ($CDCl_3$): δ = 26.9. HR MS: *m*/*z* = 291.12973 [$C_{20}H_{20}P^+$], calcd. 291.12971.

**Phosphonium Salt 8b:** Yield 95%; m.p. 149−151 °C. $^{31}P$ NMR ($CDCl_3$): δ = 16.3. HR MS: *m*/*z* = 281.10903 [$C_{18}H_{18}OP^+$], calcd. 281.10898.

**Phosphonium Salt 8c:** Yield 66%; m.p. 120−122 °C. $^{31}P$ NMR ($CDCl_3$): δ = 4.4. HR MS: *m*/*z* = 271.08822 [$C_{16}H_{16}O_2P^+$], calcd. 271.08824.

**Phosphonium Salt 8d:** Yield 74%; m.p. 116−120 °C (ref.[34] 122−123 °C). $^{31}P$ NMR ($CDCl_3$): δ = −9.6. HR MS: *m*/*z* = 261.06752 [$C_{14}H_{14}O_3P^+$], calcd. 261.06751.

**General Procedure for Wittig Reactions:** The phosphonium salt (5 mmol) was suspended under nitrogen in 50 mL of THF, and *n*BuLi or NaHMDS solution (6 mmol) was added. The mixtures were stirred for half an hour, at room temp. in the case of NaHMDS and at 0 °C in the case of *n*BuLi. After that time, clear and red to orange solutions were obtained. At −80 °C, benzaldehyde (5 mmol) was added, and the reaction mixture was allowed to warm to room temp. overnight. The mixture was heated to reflux for 3 h, the THF was evaporated, and the residue was hydrolysed with water. The mixture was extracted with $Et_2O$ (3 times, 50 mL) and dried, and the solvent was evaporated. Chromatography on silica gel with petroleum ether gave pure products **12a** and **12b**.

**Oxaphosphetane 10b:** Phosphonium salt **8d** (2 mmol), together with NaHMDS (solid, 3 mmol), were suspended in 20 mL of THF. After stirring at ambient temperature for half an hour, the mixture was cooled to −80 °C and benzaldehyde (0.2 mL) was added. The mixture was allowed to warm to 0 °C and concentrated to ca. 2 mL, and hexane (2 mL) was added. The precipitate was filtered, washed with hexane and dissolved in 10 mL of dry $CHCl_3$. This mixture was filtered off from the precipitated NaI and the obtained clear solution was concentrated at 0 °C to ca. 2 mL and allowed to crystallize at −30 °C (two weeks). The obtained colourless crystals were recrystallized from $CHCl_3$. $^1H$ NMR (400 MHz, $CDCl_3$): δ = 0.85 (dd, $^3J_{H,H}$ = 8.0, $^3J_{HP}$ = 30.0 Hz, 3 H), 4.80 (m, 1 H), 5.17 (dd, $^3J_{H,H}$ = 7.6, $^3J_{HP}$ = 7.6 Hz, 1 H), 6.47 (m, 1 H), 6.93 (d, $^3J_{H,H}$ = 3.2 Hz, 1 H), 7.20 (m, 1 H); 7.26 (m, 2 H); 7.28 (m, 2 H), 7.66 (s, 1 H). HR MS: *m*/*z* = 367.10929 [$C_{21}H_{20}O_4P^+$], calcd. 367.1094. IR (KBr): $\tilde{\nu}$ (% transmission) = 3026 (38), 1545 (35), 1493 (38), 1444 (26), 1374 (31), 1207 (26), 1132 (26), 1109 (33), 1072 (38), 1052 (39), 1011 (6), 898 (34), 884 (37), 765 (12), 755 (11), 704 (16), 694 (15), 677 (31), 639 (29), 596 (27), 566 (6), 523 (13), 458 (29), 438 $cm^{-1}$ (26).

**X-ray Crystallographic Study:** Data [λ(Mo-$K_\alpha$) = 0.71073 Å] were collected with a Bruker CCD (SMART) diffractometer. All observed reflections were used for refinement (SAINT) of the unit-cell parameters. Empirical absorption correction was carried out with SADABS.[35] The structure was solved by direct methods (SHELXTL PLUS).[36] P, O and C atoms were refined anisotropically; H atoms were refined isotropically. Table 3 lists crystallographic details. CCDC-172067 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Crystal data and structure refinement details

| | |
|---|---|
| Empirical formula | $C_{21}H_{19}O_4P$ |
| $M_r$ | 366.33 |
| Temperature [K] | 220(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| *a* [Å] | 8.729(1) |
| *b* [Å] | 17.977(2) |
| *c* [Å] | 12.048(2) |
| β [°] | 109.14(1) |
| *V* [Å$^3$] | 1785.9(3) |
| *Z* | 4 |
| $\rho_{calcd.}$ [Mg/m$^3$] | 1.362 |
| *F*(000) | 786 |
| Crystal size [mm] | 0.4 × 0.2 × 0.1 |
| Absorption coeff. [mm$^{-1}$] | 0.178 |
| 2θ range [°] | 4.24−57.62 |
| Number of reflections collected | 18296 |
| Number of indep. reflections | 4396 |
| $R_{int}$ | 0.0287 |
| Number of parameters | 305 |
| $R$ [$I > 2\sigma(I)$] | 0.0555 |
| $wR2$ (all data) | 0.1704 |
| $(\Delta/\rho)_{min.}$ [e/Å$^{-3}$] | −0.620 |
| $(\Delta/\rho)_{max}$ [e/Å$^{-3}$] | 1.085 |

## Acknowledgments

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[36] SHELXTL PLUS: Siemens Analytical X-ray Instruments Inc., **1990**; XS, Program for Crystal Structure Solution; XL, Program for Crystal Structure Refinement; XP, Interactive Molecular Graphics.

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