Structural and Spectroscopic Evidence for the Occurrence of *gauche*-Betaine Intermediates in the Thio Wittig Reaction

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Keywords: Ylides / Wittig olefination / Reaction mechanism / Phosphorus-carbon coupling constants / Substituent perturbation

Reaction of the ylide (cyclopropyl)$_3$P=CH$_2$ with Michler's thioketone S=C(C$_6$H$_4$NMe$_2$)$_2$ in [D$_5$]pyridine gave the thio Wittig intermediate [(cyclopropyl)$_3$P$^+$–CH$_2$–CAr$_2$–S$^-$] (**11**; ^{31}P NMR: δ = +27.7). Compound **11** was characterized by X-ray diffraction and shown to exhibit a *gauche*-betaine-type structure with an S–C–C–P dihedral angle of 52.9(3)° and a P···S separation of 3.312(2) Å. The characteristic averaged $^1J_{PCipso}$(aryl) coupling constant was used to elucidate the characteristic structural properties of Wittig and thio Wittig intermediates derived by treatment of the series Ph$_3$P=CH$_2$ (**2a**), Ph$_2$MeP=CH$_2$ (**2b**), and PhMe$_2$P=CH$_2$ (**2c**) with bis(*p*-methoxyphenyl) ketone to give **3** or benzophenone (to give **3′**) or bis(*p*-methoxyphenyl) thioketone (to give **5**), respectively. The oxaphosphetane series **3′a**–**3′c** shows a strong response of the $^1J_{PCipso}$(aryl) values (**3a**: 94 Hz; **3′b**: 74 Hz; **3′c**: 47 Hz) to this substituent perturbation, as it is expected for a dynamic trigonal-bipyramidal situation at the phosphorus atom, whereas the thio Wittig intermediate is only very little affected [$^1J_{PCipso}$(aryl) of **5a**: 92 Hz; **5b**: 86 Hz; **5c**: 82 Hz]. Thus, the thio Wittig intermediates **5** seem to exhibit a pronounced phosphonium character in polar solvents and may be regarded as thiabetaine-type intermediates in solution.

Introduction

The Wittig olefination reaction is among the most important preparative methods for selectively forming new carbon−carbon bonds in organic synthesis.[1] Its detailed mechanism had been a matter of controversy for some time, but now it seems to be clear that oxaphosphetanes are the essential reaction intermediates,[2] and that their betaine isomers are probably not involved at all in Wittig olefination reactions of nonstabilized ylides under the typical salt-free conditions.[3]

Thermodynamic features make the thio Wittig reaction somewhat different. The phosphorus−sulfur bond is weaker than the phosphorus−oxygen linkage, and this should make a thiaphosphetane formation less favorable than the formation of the oxaphosphetane Wittig intermediates. Thus, if betaines play any role in Wittig chemistry, they should have a chance to be detected in the reactions between phosphorus ylides and thiocarbonyl compounds. Wittig reactions of thioketones and thioaldehydes have been shown to take a kinetically different course than their ordinary ketone or aldehyde analogues in that episulfide formation can often be observed.[4] We have recently studied a representative example of a thio Wittig reaction in some detail, namely the reaction of the ylide Ph$_3$P=CH$_2$ with thiobenzophenone.[5] At 233 K in [D$_8$]toluene an intermediate (**5′a**) ("primed" numbers are used throughout this paper for the phenyl derivatives, "unprimed" numbers for the *p*-MeOC$_6$H$_4$- or *p*-Me$_2$NC$_6$H$_4$ analogues) is formed that is characterized by a ^{31}P-NMR resonance at a strongly negative δ value of −40 with coupling constants $^1J_{CC}$ = 37 Hz and $^1J_{PC}$ = 93 Hz (the corresponding ^{31}P-NMR resonance of the analogous oxaphosphetane Wittig intermediate **3′a** is at δ = −68). At 253 K the intermediate **5′a** decomposed to give the thiirane **6′** and triphenylphosphane. At 273 K these products again disappear from the solution to eventually yield the final thio Wittig products CH$_2$=CPh$_2$ (**8′**) and Ph$_3$PS (**7**).[6] The observed spectroscopic features of the intermediate **5′** are strongly solvent-dependent.[7] Successive addition of several portions of [D$_2$]dichloromethane to the solution of **5′** in [D$_8$]toluene resulted in a continuous shifting of the ^{31}P-NMR resonance from a potential thiaphosphetane range (δ = −40) to a limiting value in the phosphonium range (δ = +1 in pure CD$_2$Cl$_2$, with coupling constants $^1J_{CC}$ = 38 Hz, $^1J_{PC}$ = 82 Hz).

The model reaction Me$_3$P=CH$_2$ + S=CMe$_2$ was recently studied by an ab initio calculation.[7] A *gauche*-betaine (**9**), similar to the proposed species **5** in solution, was shown to be the essential intermediate of this reaction. Eventually we succeeded in isolating a reasonably stable example of such a *gauche*-betaine thio Wittig addition product. C−C coupling of the ylide (C$_2$H$_5$)$_3$P=CHCH$_3$ with the stabilized thioketone S=C(C$_6$H$_4$OCH$_3$)$_2$ gave **10**. Its X-ray crystal structure analysis has for the first time to our knowledge characterized a *gauche*-betaine structure of a Wittig olefination intermediate.[7]

The question has remained of whether the solid-state structure of the *gauche*-betaine **10** represents a rarely encountered or even unique example of such a species or if this type of dipolar structures is rather common in thio Wittig chemistry. It also had to be resolved whether the solution structure of the [R$_3$P−CH$_2$−CAr$_2$−S] intermediates in a polar solvent resembled the observed solid-state structure.

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[+] X-ray crystal structure analysis.

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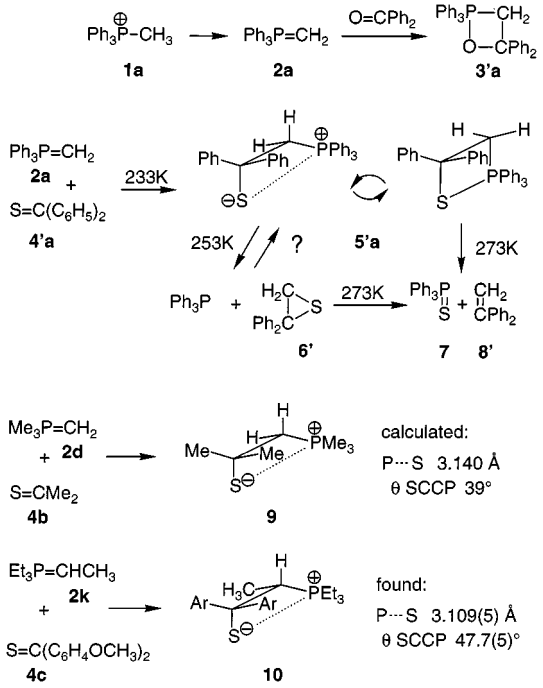


Scheme 1. Reaction paths followed in Wittig and thio Wittig reactions

In this article we present a second example of a thio Wittig *gauche*-betaine structure that was characterized by X-ray diffraction, and we will discuss a substituent-perturbation NMR study that characterizes the coordination geometry at the phosphorus atom and thus allows to better assess the structural features of the essential betaine-type intermediate of these thio Wittig reactions in solution in a polar solvent.

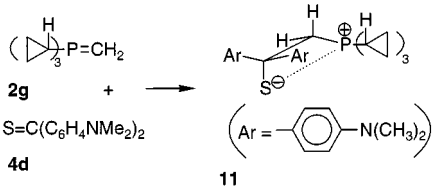
Results and Discussion

X-ray Crystal-Structure Analysis of an $R_3P^+-CH_2-CAr_2S^-$ Example

To our knowledge, I. V. Borisova et al.[8] have first proposed the formation of a betaine-type intermediate in the reaction of "thio Michler's ketone" [S=C(*p*-$Me_2N-C_6H_4)_2$ (**4d**)] with the ylide $(C_2H_5)_3P=CHCH_3$ based upon the observed ^{31}P-NMR resonance at a positive δ value of +25 (in [D_5]pyridine). The closely related *gauche*-betaine **10**, that we have prepared and characterized by X-ray diffraction (see above),[7] shows a ^{31}P-NMR resonance at δ = +28 ($^1J_{PC}$ = 71 Hz, $^3J_{PC^4Ar_2}$ = 0 and 14 Hz) in [D_5]pyridine.

We have now treated the ylide $(cyclopropyl)_3P=CH_2$, prepared by the procedure described by Schmidbaur et al.,[9] with S=C(*p*-$Me_2NC_6H_4)_2$.[10] In [D_5]pyridine solution a 1:1 mixture of the two reagents rapidly reacted at 300 K to give a single intermediate (**11**) by ylide addition to the thiocarbonyl carbon atom. Although the addition product is stable at this temperature, warming above ambient temperature results in a slow decomposition of **11** with formation of the olefination product.

At 300 K in [D_5]pyridine solution the ^{1}H-NMR spectrum of **11** shows three sets of signals of the cyclopropyl groups at the phosphorus atom [CH_2(*cis*/*trans*) at δ = 1.00/0.75; CH at δ = 1.92]. The corresponding ^{13}C-NMR signals occur at δ = 4.2 ($^2J_{PC}$ = 4.8 Hz) and δ = 4.0 ($^1J_{PC}$ = 88 Hz), and are characterized by their typical J_{PC} coupling constants.[11] The newly formed carbon−carbon single bond is characterized by ^{1}H/^{13}C-NMR CH_2 resonances at δ = 3.89 ($^2J_{PH}$ = 10 Hz)/δ = 46.4 ($^1J_{PC}$ = 72 Hz) and a quaternary carbon signal at δ = 50.8 with a $^2J_{PC}$ coupling constant of 1.8 Hz (CAr_2). In [D_5]pyridine the ^{31}P-NMR resonance of **11** is in the typical phosphonium range at δ = +27.7.



The thus prepared solution of **11** in [D_5]pyridine was oversaturated. Keeping it for ca. 2 h at 300 K resulted in the formation of single crystals of **11** that were suited for X-ray diffraction. The crystals of **11** contained one molecule of pyridine in the unit cell. The X-ray crystal structure analysis showed again that a *gauche*-betaine had resulted from the addition of an ylide (here **2g**) to a diaryl thioketone (here **4d**) (Figure 1). The newly formed carbon−carbon bond is in the expected range of a $C(sp^3)-C(sp^3)$ single bond at 1.557(4) Å (C2−C3). The adjacent C3−P4 [1.806(3) Å] and S1−C2 [1.841(3) Å] bonds are also in the respective single-bond ranges.[12] The central core of atoms is clearly nonplanar. The S1−C2−C3−P4 dihedral angle was found at θ = 52.9(3)°, and the S1···P4 separation is very large at 3.312(2) Å. Both these values are even increased as compared to the previously described first example of a *gauche*-betaine structure[7] (**10**; see above and Scheme 1). They even exceed the reported respective values [S···P 3.247 Å; θ(SCCP) = 40.9°] of the *stabilized* betaine **13** that was previously obtained upon treatment of the ylide $Ph_3P=CMe_2$ with carbon disulfide.[13]

In both structures, the bond angles at the central carbon atoms C2 and C3 are far away from 90° {**11**: C2−C3−P4: 117.6(2)° [**10**: 113.0(4)°], S1−C2−C3: 107.6(2)° [**10**: 105.9(4)°]}. The phosphonium character of the $C^3-P(C^5,C^8,C^{11})$ unit (see Figure 1) also becomes evident upon inspection of the respective bond angles around the phosphorus atom P4 of the adduct **11**. Two of the bond angles involving the C3−P4 linkage are very close to tetrahedral [C3−P4−C5: 108.5(2)°, C3−P4−C11: 107.7(2)°] whereas one is slightly larger [C3−P4−C8: 115.9(2)°]. The corresponding bond angles of the related complex **10** amount to 104.1(4)°, 116.4(5)°, and 117.6(3)°. The remaining three C−P−C angles at P4 in **11** again deviate only marginally from tetrahedral [C5−P4−C8: 108.3(2)°, C5−P4−C11: 108.9(2)°, C8−P4−C11: 107.5(2)°; **10**: 106.0(4)°, 98.7(6)°, 111.2(5)°].

These bonding features indicate a pronounced betaine-type character of **11**. Although the S1···P4 separation is still just within the sum of S and P van der Waals radii (3.6

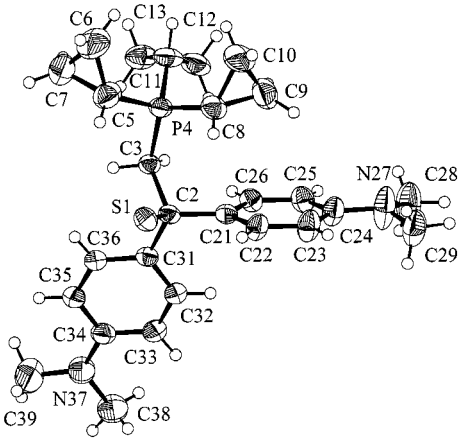
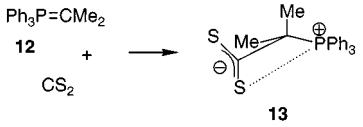


Figure 1. View of the molecular structure of the thiabetaine **11** (with unsystematical atom-numbering scheme); selected bond lengths [Å] and angles [°]: S1−C2 1.841(3), C2−C3 1.557(4), C2−C21 1.535(5), C2−C31 1.540(4), C3−P4 1.806(3), P4−C5 1.773(5), P4−C8 1.768(4), P4−C11 1.772(4), S1···P4 3.312(1); S1−C2−C3 107.6(2), S1−C2−C21 113.6(2), S1−C2−C31 109.5(2), C21−C2−C31 110.8(3), C3−C2−C21 108.4(2), C3−C2−C31 106.6(2), C2−C3−P4 117.6(2), C3−P4−C5 108.5(2), C3−P4−C8 115.9(2), C3−P4−C11 107.7(2), C5−P4−C8 108.3(2), C5−P4−C11 108.9(2), C8−P4−C11 107.5(2), S1−C2−C3−P4 52.9(3)

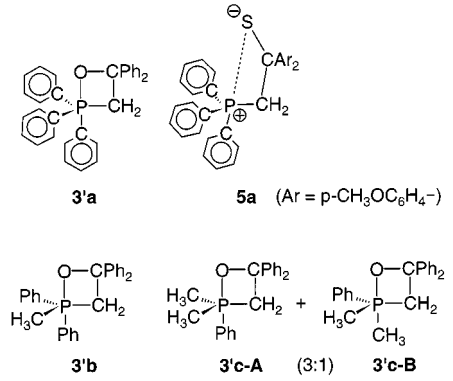


Å),[14] the observed coordination geometry at the phosphorus atom reveals that there is probably only a very small (potentially electrostatic) interaction between the negative sulfur end of the $^{-}S-C-C-P^{+}$ dipole and the strongly phosphonium-structured $C^3-P(cyclopropyl)_3$ unit of **11**. Thus, it appears that compound **11** is to be regarded as a typical example of a *gauche*-betaine-type thio Wittig intermediate. Such weakly internally stabilized *gauche*-betaine "resting stages" may possibly be more common in this area of Wittig olefination chemistry than previously thought.

NMR Evidence for the Occurrence of Betaine-Type Thio Wittig Intermediates in Solution

We were concerned whether analogous *gauche*-betaine-type structures of the thio Wittig intermediates occurred in solution in polar solvents. Could evidence be obtained to indicate that the coordination geometry of these intermediates at the phosphorus atom was substantially different from the trigonal-bipyramidal situation typically encountered with the well-established oxaphosphetanes? Monitoring the $^{1}J_{PC}$ coupling constants is a powerful tool for characterizing the structural features of the Wittig intermediates at the phosphorus atom. From a combination of X-ray crystallography[15] and NMR-spectroscopic studies[16] it is well known that the oxaphosphetane intermediates contain a trigonal-bipyramidal phosphorus atom with the oxygen atom in the apical position. In the trigonal bipyramid the $^{1}J_{PCipso}$(aryl) coupling constants of the *ipso*-carbon atoms at the aryl substituents adjacent to the phosphorus atom are very characteristically dependent on their position at the phosphorus coordination polyhedron. According to a study carried out by Vedejs and Marth[2][17] on suitable model compounds the $^{1}J_{PCipso}$(aryl) coupling constant of the apical *P*-aryl linkage in the trigonal-bipyramidal structure is rather small at values ≤ 18 Hz, whereas the corresponding $^{1}J_{PCipso}$(aryl) values of the basal P-aryl groups are much larger at ca. 130 Hz. In the oxaphosphetane **3′a** (R = Ph, see Schemes 2 and 3) a single $^{1}J_{PCipso}$(aryl) coupling constant of 94 Hz is observed experimentally. This represents an averaged value of the individual basal and apical $^{1}J_{PCipso}$ coupling constants because of a rapidly proceeding geometric equilibration, probably proceeding by means of a turnstile mechanism,[18] of the phenyl positions at the phosphorus atom, that is not frozen out on the NMR time scale at the conditions of the spectroscopic measurement. Statistical equilibration of individual $^{1}J_{PCipso}$(aryl) values close to those proposed by Vedejs et al. (see above), namely $^{1}J_{PCipso}$(aryl apical) = 18 Hz and $^{1}J_{PCipso}$(aryl basal) = 133 Hz, would be suited to adequately reproduce the observed averaged value of **3′a** and the further examples investigated in this series (**3′b**,**c**, see below).

In CD_2Cl_2 solution the alleged thiabetaine-type compound **5′a** (Ar = Ph, see Scheme 2) gives rise to an observed value of the $^{1}J_{PCipso}$(aryl) coupling constant of 92 Hz. This very close similarity between the $^{1}J_{PCipso}$(aryl) values of the oxaphosphetane **3′a** and the thiabetaine **5′a** led to the concern that this might indicate the presence of a pentacoordinate coordination geometry in **5′a**, and thus might suggest a strong P−S interaction in solution even when polar solvents were used.



Scheme 2. Structures of compounds used in the substituent perturbation study

However, it must be pointed out that due to the rapid pseudo-rotational equilibration that leads to averaging of the extremely different $^{1}J_{PCipso}$(aryl basal/apical) coupling constants, a differentation between pentacoordinate trigonal-bipyramidal and tetracoordinate tetrahedral geometries at the phosphorus atom by means of the observed coupling constants is not possible in the Ph_3P-derived cases: Both situations would provide very similar averaged $^{1}J_{PCipso}$(aryl) values, as is actually found for the **3′a**/**5′a** pair

of compounds. It is evident from this analysis that a clear differentiation should occur if one or two of the aryl substituents at the phosphorus atom were replaced by alkyl groups. Such a substituent perturbation should lead to clearly different expected averaged $^1J_{PC\mathit{ipso}}$(aryl) coupling constants for the two extreme geometric coordinative situations at the phosphorus center, the trigonal-bipyramidal or the tetrahedral one. We, therefore, have prepared several series of "alkyl-perturbed" analogues[19] of **3a** and **5a** and compared the response of the respective $^1J_{PC\mathit{ipso}}$(aryl) values on the number of alkyl groups introduced. This has led to a rather clear structural distinction between the compounds **3** and **5** in solution.

Treatment of Ph_2PCl with methyllithium followed by electrophilic methylation and treatment with base furnished the ylide $Ph_2MeP{=}CH_2$ (**2b**). Its reaction with bis(*p*-methoxyphenyl) ketone or benzophenone gave the oxaphosphetanes **3b** and **3′b**, respectively; treatment of **2b** with bis(*p*-methoxyphenyl) thioketone generated **5b**. The ylide $PhMe_2P{=}CH_2$ (**2c**) was prepared analogously starting from $PhPCl_2$. Subsequent treatment with $O{=}CAr_2$ or $S{=}CAr_2$ gave **3c**, **3′c**, or **5c**, respectively.

The observed $^1J_{PC\mathit{ipso}}$(aryl) coupling constants of the oxaphosphetane **3′b** is 74 Hz. This is the expected basal/apical averaged value using the Vedejs′ values of $^1J_{PC\mathit{ipso}}$(basal) ≈ 133 Hz and $^1J_{PC\mathit{ipso}}$(apical) ≈ 18 Hz (see above).[17] Apparently, a dynamic structural situation is found for **3′b** where one of the phenyl groups is predominately oriented in the apical position *trans* to the oxaphosphetane oxygen atom. The observed $^1J_{PC\mathit{ipso}}$(aryl) coupling constant of the oxaphosphetane **3′c** is much smaller at 47 Hz. Assuming the same individual $^1J_{PC\mathit{ipso}}$(aryl) coupling constants for basal and apical phenyl substituents at the phosphorus atom as above, namely 133 Hz and 18 Hz, this would indicate a dynamic equilibration of the two major pseudorotamers **3′c-A** and **3′c-B** (see Scheme 2) in a 3:1 equilibrium ratio. Thus, perturbing the substituent pattern at the phosphorus atom in the oxaphosphetanes **3′** by formally exchanging phenyl for methyl groups has a very pronounced effect on the turnstile-averaged $^1J_{PC\mathit{ipso}}$(aryl) coupling constant: It is reduced from 94 Hz in **3′a** consecutively to 74 Hz (in **3′b**) and 47 Hz (in **3′c**). An analogous trend is observed in the *p*-methoxyphenyl series **3(b,c)** (see Experimental Section). Thus, a continuous reduction of the averaged $^1J_{PC\mathit{ipso}}$(aryl) coupling constant is a direct consequence of the structural and dynamic features of the trigonal-bipyramidal geometry of the pentacoordinate phosphorus atom in the oxaphosphetanes, and this alkyl-perturbation effect may therefore be used as an analytical indicator of the structural situation specifically encountered here.

The response of the thio Wittig intermediate **5** to the substituent perturbation at the phosphorus atom is quite different. Introducing one or two methyl groups has only a very small effect on the observed $^1J_{PC\mathit{ipso}}$(aryl) coupling constant. For **5a** we observe a value of 92 Hz, for **5b** and **5c** this value is only slightly smaller at 86 Hz and 82 Hz, respectively. A comparison with the respective $^1J_{PC\mathit{ipso}}$(aryl) values of the corresponding phosphonium salts (**1**) or phosphorus ylides (**2**, see Table 1; for a comparison of additional selected NMR-spectroscopic features of these series of compounds, see Tables 2 and 3) indicates that the phosphorus center in compounds **5** seems to exhibit a behavior as it is grossly expected for a close to tetracoordinated tetrahedral geometry. Two additional series of related "alkyl-perturbed" oxaphosphetanes and thiabetaines were prepared introducing cyclopropyl (**3′/5e−g**) or ethyl substituents (**3/5h−k**) at the phosphorus atom. In the **3/5h** systems the NMR resonances of a pair of diastereotopic aryl substituents are observed at the phosphorus atom even under the here encountered nonstatic conditions due to the chirality center at the adjacent carbon atom C3.

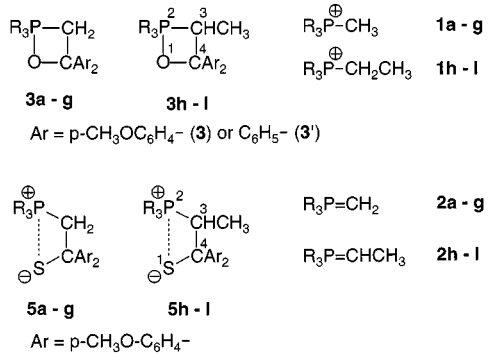
Their $^1J_{PC\mathit{ipso}}$(aryl) response is analogous as it was observed in the **(3)3′/5a−c** series described above. Thus, it seems that the structures of the thio Wittig intermediates **5** in solution are markedly different from those of the oxaphosphetane intermediates **3** of the parent Wittig olefination reaction, here starting from an ordinary diaryl ketone. The response of the relevant structural indicator

Table 1. Comparison of ^{31}P-NMR chemical shifts and $^1J_{(PC\mathit{ipso})}$(aryl) coupling constants of **3**, **5**, **1** and **2**

		Oxaphosphetane **3** (**3′**)[a]		Thiabetaine **5**		Phosphonium salt **1**		Ylide **2**	
R_3P	Compd.	$\delta^{31}P$[c]	$^1J_{PC\mathit{ipso}}$(aryl)[i]	$\delta^{31}P$[e]	$^1J_{PC\mathit{ipso}}$(aryl)[i]	$\delta^{31}P$[f]	$^1J_{PC\mathit{ipso}}$(aryl)[i]	$\delta^{31}P$[g]	$^1J_{PC\mathit{ipso}}$(aryl)[i]
Ph_3P	**a**	(−68)	(94)	5[d]/−40[b,l]	92[b,k]	22	88	21	85
$MePh_2P$	**b**	(−76)	(76)	2	86	20	89	11	78
Me_2PhP	**c**	(−85)	(47)	9	82	21	88	4	66
Me_3P	**d**	(−88)	–	11	–	23	–	−3	–
(cyclopropyl)Ph_2P	**e**	(−67)	(71)	14	86	30	89	26	88
(cyclopropyl)$_2$PhP	**f**	(−70)	(33)	17	101	36	89	31	90
(cyclopropyl)$_3$P	**g**	−69	–	33	–	43	–	36	–
$EtPh_2P$	**h**	−63	47/89	14	68/88	33	82	16	74
Et_2PhP	**i**	−65	24	25	77	37	80	18	65
Et_3P	**k**	−66	–	27	–	41	–	18	–
Ph_3P	**l**	(−61)	(94)	[h]	[h]	[h]	[h]	[h]	[h]

[a] **3**: Derived from $(p\text{-}CH_3OC_6H_4)_2CO$; **3′** derived from Ph_2CO (in parentheses). – [b] Values for **5′a**, derived from Ph_2CS. – [c] In [D$_8$]THF. – [d] In CD_2Cl_2. – [e] In [D$_5$]pyridine. – [f] In $CDCl_3$. – [g] In [D$_6$]benzene. – [h] Not determined. – [i] $^1J_{PC\mathit{ipso}}$(aryl) in Hz, for structures see Scheme 3. – [k] Broad signal. – [l] In [D$_8$]toluene.

$^1J_{PC\,ipso}$(aryl) points to a pronounced phosphonium character of the thio Wittig intermediates **5** under the applied conditions. In view of the structural results obtained for two representative examples in the solid state by X-ray diffraction, these NMR observations make it likely that *gauche*-thiabetaines may also be the favored structural types of the thio Wittig intermediates in solution in sufficiently polar solvents.



Scheme 3. Structures of the compounds listed in Tables 1−3

Experimental Section

General Remarks: All reactions involving air-sensitive compounds were carried out under argon in a glove box or using Schlenk-type glassware. Solvents (including deuterated solvents) were dried and distilled under argon prior to use (THF: sodium/potassium alloy; [D_5]pyridine, [D_2]dichloromethane: calciumhydride). Trimethylphosphane, the chlorophosphanes, cyclopropyl bromide, 1.6 M methyllithium solution in diethyl ether and 4,4′-dimethoxybenzophenone were purchased from commercial sources. Cyclopropyllithium,[20] the phosphanes,[21−25] the phosphonium salts,[22,26−29] the ylides[29−35] and the thioketone[36] were prepared according to literature procedures. NMR experiments were performed with a Bruker AC 200 P FT-NMR spectrometer (^{1}H: 200.1 MHz; ^{31}P: 81.0 MHz; ^{13}C: 50.3 MHz), a Bruker AM 360 spectrometer (^{1}H: 360.1 MHz; ^{13}C: 90.6 MHz) and with a Varian Unity Plus 600 spectrometer (^{1}H: 599.9 MHz; ^{31}P: 242.9 MHz; ^{13}C: 150.8 MHz). The assignments in the ^{1}H- and ^{13}C-NMR spectra of selected examples were confirmed through GCOSY, GHSQC, and GHMBC spectra[37] (atom-numbering scheme used as depicted in Scheme 3). IR spectra were acquired with a Nicolet 5 DXC Fourier transform IR spectrometer. Melting points were obtained by differential scanning calorimetry (DSC 2010, TA Instruments); elemental analyses were determined with a Foss-Heraeus CHN-rapid elemental analyzer.

Table 2. Selected ^{13}C-NMR data of **3** and **5**

R_3P	Oxaphosphetane **3/3′**[a] Compd.[b]	δ(C_{ipso})[c]	δC-3	^1J(PC-3)[d]	δ(C^4Ar_2)[e]	^3J(PC^4Ar_2)[d,e]	Thiabetaine **5**[f] Compd.	δ(C_{ipso})[c]	δC-3	^1J(PC-3)[d]	δ(C^4Ar_2)[e]	^3J(PC^4Ar_2)[d,e]
Ph_3P	**3′a**	143	66	87	151	6.9	**5′a**	133[g]	65	93	152	8.6
							5a	127[h]	52	82	144	7.4
$MePh_2P$	**3′b**	148	68	87	152	6.9	**5b**	130	52	79	147	8.3
Me_2PhP	**3′c**	152	67	90	152	6.9	**5c**	129	51	74	147	8.9
Me_3P	**3′d**	–	65	89	153	8.2	**5d**	–	49	75	147	8.3
(cyclopropyl)Ph_2P	**3′e**	148	65	90	151	6.9	**5e**	127	52	78	147	8.4
(cyclopropyl)$_2$PhP	**3′f**	154	67	97	151	6.9	**5f**	129[h]	49	81	147	8.2
(cyclopropyl)$_3$P	**3g**	–	59	94	144	6.9	**5g**	–	46	72	148	9.1
$EtPh_2P$	**3h**	149/144	68	93	145/140	9.0/4.9	**5h**	124/122[h]	58	72	147/143	1.0/14.0
Et_2PhP	**3i**	149	69	95	145/140	6.9/5.6	**5i**	126	53	67	148/144	0/13.7
Et_3P	**3k**	–	64	90	146/141	6.9/6.4	**10**	–	49	68	148/144	0/12.9
Ph_3P	**3′l**	**143**	**70**	**89**	151/146	12.5/2.8						

[a] In [D_8]THF. – [b] **3′a**−**f** and **l** derived from Ph_2CO, **3g**−**k** from (p-$CH_3OC_6H_4)_2CO$. – [c] P(Ar)-*ipso*-C. – [d] Coupling constants in Hz. – [e] *ipso*-C of the aryl groups at C-4, chemical shift and ^3J(PC) coupling constant. – [f] In [D_5]pyridine. – [g] In [D_8]toluene. – [h] In CD_2Cl_2.

Table 3. Selected ^{13}C-NMR data of **1** and **2** for comparison

R_3P	Compd.	Phosphonium salt **1**[a] δ(C_{ipso})[b]	δC_{alkyl}	$^1J_{PCalkyl}$[c]	Ylide **2**[d] δ(C_{ipso})[b]	$\delta_{C=P}$	$^1J_{(P=C)}$[c]
Ph_3P	**a**	118	11	57	135	−4	100
$MePh_2P$	**b**	119	10	58	137	−5	97
Me_2PhP	**c**	120	11	56	140	−6	96
Me_3P	**d**	–	8	56	–	[e]	[e]
(cyclopropyl)Ph_2P	**e**	119	10	58	136	−15	109
(cyclopropyl)$_2$PhP	**f**	119	7	59	135	−23	112
(cyclopropyl)$_3$P	**g**	–	3	61	–	−14	114
$EtPh_2P$	**h**	117	15	50	135	−2	117
Et_2PhP	**i**	116	13	50	135	−7	117
Et_3P	**k**	–	12	49	–	[e]	[e]

[a] In $CDCl_3$. – [b] P(Ar)-*ipso*-C. – [c] Coupling constants in Hz. – [d] In [D_6]benzene. – [e] Not determined.

Dicyclopropyl(phenyl)phosphane: Treatment of 70 mL (64.4 mmol) of a 0.92 M solution of cyclopropyllithium in diethyl ether with 4.0 g (3.0 mL, 22.1 mmol) of dichloro(phenyl)phosphane in 20 mL of diethyl ether yielded 3.2 g (76%) of dicyclopropyl(phenyl)phosphane. − ^{1}H NMR (200.1 MHz, 300 K, [D$_6$]benzene): δ = 7.72 (m, 2 H, *m*-H, Ph), 7.23 (m, 3 H, *p*-, *o*-H, Ph), 0.83 (m, 2 H, PCH), 0.64 (m, 8 H, CH_2). − ^{13}C NMR (50.3 MHz, 300 K, [D$_6$]benzene): δ = 142.2 (d, *i*-C, $^1J_{PC}$ = 10.7 Hz), 131.5 (d, *o*-C, $^2J_{PC}$ = 15.3 Hz), 128.4 (d, *m*-C, $^3J_{PC}$ = 5.4 Hz), 128.0 (s, *p*-C, $^4J_{PC}$ = 0 Hz), 7.9 (d, PCH, $^1J_{PC}$ = 4.1 Hz), 4.1 (d, CH_2, $^2J_{PC}$ = 11.6 Hz), 3.9 (d, CH_2, $^2J_{PC}$ = 12.4 Hz). − ^{31}P NMR (81.0 MHz, 300 K, [D$_6$]benzene): δ = 10.3.

(Cyclopropyl)(methyl)diphenylphosphonium Iodide (1e): Treatment of 3.4 g (15.2 mmol) of (cyclopropyl)diphenylphosphane with 2.2 g (1.1 mL, 15.5 mmol) of methyl iodide in 20 mL of diethyl ether for 2 d at room temperature yielded 5.3 g (95%) of the phosphonium salt. − ^{1}H NMR (360.1 MHz, 303 K, $CDCl_3$): δ = 7.83 (m, 4 H, *o*-H, Ph), 7.73 (m, 2 H, *p*-H, Ph), 7.63 (m, 4 H, *m*-H, Ph), 2.70 (d, 3 H, PCH_3, $^2J_{PH}$ = 13.3 Hz), 2.40 (m, 1 H, PCH), 1.48, 0.81 (m, each 2 H, CH_2). − ^{13}C NMR (50.3 MHz, 300 K, $CDCl_3$): δ = 134.7 (d, *p*-C, $^4J_{PC}$ = 3.3 Hz), 132.7 (d, *o*-C, $^2J_{PC}$ = 9.9 Hz), 130.0 (d, *m*-C, $^3J_{PC}$ = 13.2 Hz), 118.6 (d, *i*-C, $^1J_{PC}$ = 89.1 Hz), 9.5 (d, CH_3, $^1J_{PC}$ = 57.7 Hz), 4.9 (d, CH_2, $^2J_{PC}$ = 5.0 Hz), 1.8 (d, PCH, $^1J_{PC}$ = 85.8 Hz). − ^{31}P NMR (81.0 MHz, 300 K, $CDCl_3$): δ = 29.5. − IR (KBr): ṽ = 3012, 2975, 2934, 2881, 1586, 1484, 1436, 1328, 1196, 1170, 1117, 894, 755, 755, 663 cm^{-1}. − $C_{13}H_{18}PI$ (368.20): calcd. C 52.19, H 4.93; found C 52.09, H 4.92. − M.p. 154°C.

Dicyclopropyl(methyl)(phenyl)phosphonium Iodide (1f): Treatment of 3.3 g of (17.2 mmol) dicyclopropyl(phenyl)phosphane with 2.9 g (1.3 mL, 20.6 mmol) of methyl iodide in 20 mL of diethyl ether for 2 d at room temperature yielded 5.3 g (93%) of the phosphonium salt. − ^{1}H NMR (200.1 MHz, 300 K, $CDCl_3$): δ = 7.94 (m, 2 H, *o*-H, Ph), 7.62 (m, 3 H, *p*-, *m*-H, Ph), 2.27 (d, 3 H, PCH_3, $^2J_{PH}$ = 13.2 Hz), 1.82 (m, 2 H, PCH), 1.32 (m, 4 H, CH_2), 1.02 (m, 4 H, CH_2). − ^{13}C NMR (50.3 MHz, 300 K, $CDCl_3$): δ = 134.6 (d, *p*-C, $^4J_{PC}$ = 3.3 Hz), 132.2 (d, *o*-C, $^2J_{PC}$ = 9.1 Hz), 130.0 (d, *m*-C, $^3J_{PC}$ = 12.4 Hz), 118.6 (d, *i*-C, $^1J_{PC}$ = 89.1 Hz), 7.4 (d, CH_3, $^1J_{PC}$ = 59.4 Hz), 4.8 (d, CH_2, $^2J_{PC}$ = 5.0 Hz), 4.4 (d, CH_2, $^2J_{PC}$ = 5.0 Hz), 1.1 (d, PCH, $^1J_{PC}$ = 87.4 Hz). − ^{31}P NMR (81.0 MHz, 300 K, $CDCl_3$): δ = 35.7. − IR (KBr): ṽ = 3070, 2969, 2939, 2882, 1440, 1315, 1192, 1117, 1047, 913, 821, 757, 696 cm^{-1}. − $C_{13}H_{18}PI$ (332.16): calcd. C 47.01, H 5.46; found C 47.03, H 5.45. − M.p. 119°C.

(Cyclopropyl)(methylene)diphenylphosphorane (2e): Treatment of 2.24 g (6.08 mmol) of (cyclopropyl)(methyl)diphenylphosphonium iodide with 0.36 g of KH (8.98 mmol) in 10 mL of THF for 2 h at room temperature yielded 1.30 g (89%) of the ylide as wax-like solid. − ^{1}H NMR (200 MHz, 300 K, [D$_6$]benzene): δ = 7.87 (m, 4 H, *o*-H, Ph), 7.08 (m, 6 H, *p*-, *m*-H, Ph), 1.05 (m, 2 H, PCH), 0.92 (m, 4 H, CH_2), 0.46 (m, 4 H, CH_2), −0.02 (d, 2 H, P=CH_2, $^2J_{PH}$ = 8.7 Hz). − ^{13}C NMR (50.3 MHz, 300 K, [D$_6$]benzene): δ = 135.8 (d, *i*-C, $^1J_{PC}$ = 87.5 Hz), 131.9 (d, *o*-C, $^2J_{PC}$ = 8.4 Hz), 130.6 (s, *p*-C, $^4J_{PC}$ = 0 Hz), 128.4 (d, *m*-C, $^3J_{PC}$ = 11.7 Hz), 6.6 (d, CH, $^1J_{PC}$ = 78.2 Hz), 1.5 (d, CH_2, $^2J_{PC}$ = 3.0 Hz), −14.8 (d, P=CH_2, $^1J_{PC}$ = 108.9 Hz). − ^{31}P NMR (81.0 MHz, 300 K, [D$_6$]benzene): δ = 25.9. − IR (KBr): ṽ = 3060, 3007, 1484, 1436, 1294, 1196, 1112, 933, 893, 741, 711 cm^{-1}. − M.p. 45°C.

Dicyclopropyl(methylene)(phenyl)phosphorane (2f): Treatment of 2.55 g (7.68 mmol) of dicyclopropyl(methyl)(phenyl)phosphonium iodide with 0.46 g (11.47 mmol) of KH in 10 mL of THF for 2 h at room temperature yielded 1.45 g (93%) of the ylide as a pale yellow liquid. − ^{1}H NMR (200.1 MHz, 300 K, [D$_6$]benzene): δ = 7.91 (m, 2 H, *o*-H, Ph), 7.16 (m, 3 H, *p*-, *m*-H, Ph), 0.78 (m, 4 H, CH_2), 0.62 (m, 2 H, PCH), 0.43 (m, 4 H, CH_2), −0.59 (d, 2 H, P=CH_2, $^2J_{PH}$ = 9.1 Hz). − ^{13}C NMR (50.3 MHz, 300 K, [D$_6$]benzene): δ = 135.3 (d, *i*-C, $^1J_{PC}$ = 90.1 Hz), 131.4 (d, *p*-C, $^4J_{PC}$ = 2.4 Hz), 130.7 (d, *o*-C, $^2J_{PC}$ = 7.9 Hz), 128.3 (d, *m*-C, $^3J_{PC}$ = 11.0 Hz), 7.4 (d, CH, $^1J_{PC}$ = 83.6 Hz), 1.8 (d, CH_2, $^2J_{PC}$ = 3.1 Hz), 1.3 (d, CH_2, $^2J_{PC}$ = 3.1 Hz), −21.8 (d, P=CH_2, $^1J_{PC}$ = 112.9 Hz). − ^{31}P NMR (81.0 MHz, 300 K, [D$_6$]benzene): δ = 31.4. − IR (KBr): ṽ = 3091, 3004, 1499, 1438, 1302, 1177, 1037, 949, 899, 749, 696 cm^{-1}. − M.p. 8°C.

(Ethyl)(ethylidene)diphenylphosphorane (2h): 4.7 mL (7.52 mmol) of a 1.6 M BuLi solution in hexane was slowly added to a suspension of 2.50 g (7.73 mmol) of diethyldiphenylphosphonium bromide in 10 mL of THF at 0°C. After 30 min, the reaction was complete. The solvent was removed in vacuo and the ylide was purified by vacuum transfer to give 1.65 g (90%) of a red, highly viscous liquid. − ^{1}H NMR (200.1 MHz, 300 K, [D$_6$]benzene): δ = 7.64 (m, 4 H, *o*-H, Ph_2P), 7.08 (m, 6 H, *m*-, *p*-H, Ph_2P), 2.05 (dd, 3 H, PCHCH_3, $^3J_{PH}$ = 18.8 Hz, $^3J_{HH}$ = 6.7 Hz), 1.92 (dq, 2 H, CH_2CH$_3$, $^2J_{PH}$ = 11.9 Hz, $^3J_{HH}$ = 7.5 Hz), 1.00 (dt, 3 H, CH_2CH_3, $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 7.5 Hz), 0.67 (dq, 2 H, P=C*H*CH$_3$, $^2J_{PH}$ = 13.6 Hz, $^3J_{HH}$ = 6.7 Hz). − ^{13}C NMR (50.3 MHz, 300 K, [D$_6$]benzene): δ = 134.6 (d, *i*-C, Ph_2P, $^1J_{PC}$ = 74.2 Hz), 132.3 (d, *o*-C, $^2J_{PC}$ = 9.9 Hz), 130.3 (d, *p*-C, $^4J_{PC}$ = 3.3 Hz), 128.6 (d, *m*-C, $^3J_{PC}$ = 9.9 Hz), 19.9 (d, PCH_2, $^1J_{PC}$ = 64.3 Hz), 10.7 (d, PCH*C*H$_3$, $^2J_{PC}$ = 5.0 Hz), 7.0 (d, PCH_2*C*H$_3$, $^2J_{PC}$ = 3.3 Hz), −1.8 (d, P=CH, $^1J_{PC}$ = 117.1 Hz). − ^{31}P NMR (81.0 MHz, 300 K, [D$_6$]benzene): δ = 16.2. − IR (KBr): ṽ = 3067, 2980, 2926, 2894, 2829, 1451, 1440, 1180, 1105, 830, 753, 696 cm^{-1}.

Diethyl(ethylidene)(phenyl)phosphorane (2i): 4.2 mL (6.72 mmol) of a 1.6 M BuLi solution in hexane was slowly added to a suspension of 2.00 g (7.27 mmol) of triethyl(phenyl)phosphonium bromide in 10 mL of THF at 0°C. After 30 min, the reaction was complete. The solvent was removed in vacuo and the phosphorane was purified by vacuum transfer to give 1.29 g (97%) of a light red viscous liquid. − ^{1}H NMR (360.1 MHz, 303 K, [D$_6$]benzene): δ = 7.67 (m, 2 H, *o*-H, PhP), 7.19 (m, 3 H, m, *p*-H, PhP), 2.09 (br. s, 3 H, PCHCH_3, $^3J_{PH}$, $^3J_{HH}$ not resolved), 1.55 (br. s, 4 H, PCH_2CH$_3$, $^2J_{PH}$, $^3J_{HH}$ not resolved), 0.93 (br. s, 6 H, PCH_2CH_3, $^3J_{PH}$, $^3J_{HH}$ not resolved), 0.36 (br. s, 1 H, P=C*H*CH$_3$, $^2J_{PH}$, $^3J_{HH}$ not resolved). − ^{13}C NMR (90.6 MHz, 303 K, [D$_6$]benzene): δ = 135.4 (d, *i*-C, $^1J_{PC}$ = 65.2 Hz), 132.0 (d, *o*-C, $^2J_{PC}$ = 8.4 Hz), 130.3 (d, *p*-C, $^4J_{PC}$ = 3.2 Hz), 128.5 (d, *m*-C, $^3J_{PC}$ = 10.5 Hz), 19.6 (d, PCH_2, $^1J_{PC}$ = 58.9 Hz), 10.7 (br. s, PCH*C*H$_3$, $^2J_{PC}$ not resolved), 7.0 (br. s, PCH_2*C*H$_3$, $^2J_{PC}$ not resolved), −6.8 (d, P=CH, $^1J_{PC}$ = 116.8). − ^{31}P NMR (81.0 MHz, 300 K, [D$_6$]benzene): δ = 17.7. − IR (KBr): ṽ = 2973, 2926, 2908, 2880, 2831, 1458, 1443, 1410, 1388, 1284, 1173, 1101, 1051, 832, 777, 690 cm^{-1}.

Generation of the Wittig and Thio Wittig Intermediates. − General Description of the NMR Experiments: In a typical NMR experiment the phosphorus ylide was given into a 5-mm NMR tube and dissolved in ca. 0.2 mL of solvent, fitted with a rubber septum and kept at −78°C (−35°C for pyridine samples) for at least 10 min. Into this NMR tube the solution of the benzophenone derivative in ca. 0.4 mL of solvent was injected by syringe. Under these conditions the two phases mixed slowly. The system was allowed to thermally equilibrate for a period of 10 min before it was quickly shaken three times outside the cooling bath. Then the in situ formed Wittig and thio Wittig intermediates were characterized by NMR spectroscopy. For the description of the obtained NMR spectra the atom-numbering schemes as shown in Scheme 3 were used.

***P,P,P*,4,4-Pentaphenyl-1,2-oxaphosphetane (3′a):** 22 mg (80 μmol) of (methylene)triphenylphosphorane was treated with 15 mg (82 μmol) of benzophenone in ca. 0.6 mL of [D$_8$]THF at −78°C. − ^{1}H NMR (360.1 MHz, 243 K, [D$_8$]THF): δ = 7.45 (m, 4 H, *o*-H, Ph), 7.42 (m, 3 H, *p*-H, Ph$_3$P), 7.37 (m, 6 H, *m*-H, Ph$_3$P), 7.17 (m, 6 H, *o*-H, Ph$_3$P), 7.11 (m, 4 H, *m*-H, Ph), 7.01 (m, 2 H, *p*-H, Ph), 5.23 (d, 2 H, PCH$_2$, $^2J_{PH}$ = 16.5 Hz). − ^{13}C NMR (90.6 MHz, 243 K, [D$_8$]THF): δ = 151.0 (d, *i*-C, Ph, $^3J_{PC}$ = 6.9 Hz), 143.4 (d, *i*-C, Ph$_3$P, $^1J_{PC}$ = 94.3 Hz), 133.2 (d, *o*-C, Ph$_3$P, $^2J_{PC}$ = 9.7 Hz), 129.1 (s, *p*-C, Ph$_3$P, $^4J_{PC}$ = 0 Hz), 128.3 (*m*-C, Ph), 128.1 (d, *m*-C, Ph$_3$P, $^3J_{PC}$ = 12.5 Hz), 126.5 (*o*-C, Ph), 126.2 (*p*-C, Ph), 71.1 (d, C-4, $^2J_{PC}$ = 13.9 Hz), 66.0 (d, C-3, $^1J_{PC}$ = 87.4 Hz). − ^{31}P NMR (81.0 MHz, 243 K, [D$_8$]THF): δ = −68.3.

***P*-Methyl-*P,P*,4,4-tetraphenyl-1,2-oxaphosphetane (3′b):** 50 mg (233 μmol) of (methyl)(methylene)diphenylphosphorane was treated with 43 mg (236 μmol) of benzophenone in 740 mg of [D$_8$]THF at −78°C. − ^{1}H NMR (360.1 MHz, 243 K, [D$_8$]THF): δ = 7.58 (m, 4 H, *o*-H, Ph), 7.30 (d, 4 H, *o*-H, Ph$_2$P), 7.23 (m, 4 H, *m*-H, Ph), 7.19 (m, 6 H, *m*-, *p*-H, Ph$_2$P), 7.10 (d, 2 H, *p*-H, Ph), 4.66 (d, 2 H, PCH$_2$, $^2J_{PH}$ = 17.2 Hz), 2.23 (d, 3 H, PCH$_3$, $^2J_{PH}$ = 14.2 Hz). − ^{13}C NMR (90.6 MHz, 243 K, [D$_8$]THF): δ = 151.6 (d, *i*-C, Ph, $^3J_{PC}$ = 6.9 Hz), 148.0 (d, *i*-C, Ph$_2$P, $^1J_{PC}$ = 73.5 Hz), 131.6 (d, *o*-C, Ph, $^2J_{PC}$ = 9.7 Hz), 128.7 (br. s, *p*-C, Ph$_2$P, $^4J_{PC}$ < 1 Hz), 128.6 (*m*-C, Ph), 128.1 (*m*-C, Ph$_2$P, $^3J_{PC}$ = 9.7 Hz), 126.5 (*o*-C, Ph), 126.4 (*p*-C, Ph), 70.5 (d, C-4, $^2J_{PC}$ = 13.9 Hz), 67.5 (d, C-3, $^1J_{PC}$ = 87.4 Hz), 21.8 (d, PCH$_3$, $^1J_{PC}$ = 97.1 Hz). − ^{31}P NMR (81.0 MHz, 243 K, [D$_8$]THF): δ = −75.5.

4,4-Bis(4′-methoxyphenyl)-*P*-methyl-*P,P*-diphenyl-1,2-oxaphosphetane (3b): 21 mg (98 μmol) of (methyl)(methylene)diphenylphosphorane was treated with 27 mg (111 μmol) of bis(*p*-methoxyphenyl) ketone in ca. 0.6 mL of [D$_8$]THF at −78°C. − ^{1}H NMR (360.1 MHz, 243 K, [D$_8$]THF): δ = 7.50 (m, 4 H, *o*-H, Ph$_2$P), 7.43 (d, 4 H, *o*-H, Ph, $^3J_{HH}$ = 8.7 Hz), 7.31 (m, 2 H, *p*-H, Ph$_2$P), 7.26 (m, 4 H, *m*-H, Ph$_2$P), 6.78 (d, 4 H, *m*-H, Ph, $^3J_{HH}$ = 8.7 Hz), 4.55 (d, 2 H, PCH$_2$, $^2J_{PH}$ = 17.4 Hz), 3.70 (s, 6 H, OCH$_3$), 2.23 (d, 3 H, PCH$_3$, $^2J_{PH}$ = 14.5 Hz). − ^{13}C NMR (90.6 MHz, 243 K, [D$_8$]THF): δ = 158.5 (*p*-C, Ph), 148.5 (d, *i*-C, Ph$_2$P, $^1J_{PC}$ = 76.3 Hz), 143.9 (d, *i*-C, Ph, $^3J_{PC}$ = 7.0 Hz), 131.7 (d, *o*-C, Ph$_2$P, $^2J_{PC}$ = 8.2 Hz), 128.6 (s, *p*-C, Ph$_2$P, $^4J_{PC}$ = 0 Hz), 128.1 (d, *m*-C, Ph$_2$P, $^3J_{PC}$ = 10.6 Hz), 127.4 (*o*-C, Ph), 113.5 (*m*-C), 69.8 (d, C-4, $^2J_{PC}$ = 15.3 Hz), 67.7 (d, C-3, $^1J_{PC}$ = 88.6 Hz), 55.1 (OCH$_3$), 21.6 (d, PCH$_3$, $^1J_{PC}$ = 96.3 Hz). − ^{31}P NMR (81.0 MHz, 243 K, [D$_8$]THF): δ = −76.3.

***P,P*-Dimethyl-*P*,4,4-triphenyl-1,2-oxaphosphetane (3′c):** 39 mg (256 μmol) of dimethyl(methylene)(phenyl)phosphorane was treated with 46 mg (253 μmol) of benzophenone in 690 mg of [D$_8$]THF at −78°C. − ^{1}H NMR (360.1 MHz, 243 K, [D$_8$]THF): δ = 7.57 (m, 4 H, *o*-H, Ph), 7.48 (d, 2 H, *o*-H, PhP), 7.22 (m, 7 H, *m*-H, Ph, *m*- and *p*-H, PhP), 7.08 (m, 2 H, *p*-H, Ph), 4.43 (d, 2 H, PCH$_2$, $^2J_{PH}$ = 17.1 Hz), 1.81 (d, 3 H, PCH$_3$, $^2J_{PH}$ = 13.1 Hz). − ^{13}C NMR (90.6 MHz, 243 K, [D$_8$]THF): δ = 152.2 (d, *i*-C, Ph, $^3J_{PC}$ = 6.9 Hz), 151.6 (d, *i*-C, PhP, $^1J_{PC}$ = 47.2 Hz), 129.5 (d, *o*-C, Ph, $^2J_{PC}$ = 8.3 Hz), 128.43 (obscured, *m*-C, PhP, $^3J_{PC}$ not determined), 128.4 (*m*-C, Ph), 128.2 (br. s, *p*-C, PhP, $^4J_{PC}$ not resolved), 126.5 (*o*-C, Ph), 126.2 (*p*-C, Ph), 70.3 (d, C-4, $^2J_{PC}$ = 13.9 Hz), 67.0 (d, C-3, $^1J_{PC}$ = 90.2 Hz), 22.4 (d, PCH$_3$, $^1J_{PC}$ = 84.6 Hz). − ^{31}P NMR (81.0 MHz, 243 K, [D$_8$]THF): δ = −83.9.

4,4-Bis(4′-methoxyphenyl)-*P,P*-dimethyl-*P*-phenyl-1,2-oxaphosphetane (3c): 15 mg (99 μmol) of dimethyl(methylene)(phenyl)phosphorane was treated with 24 mg (99 μmol) of 4,4′-dimethoxybenzophenone in ca. 0.6 mL of [D$_8$]THF at −78°C. − ^{1}H NMR (360.1 MHz, 243 K, [D$_8$]THF): δ = 7.49 (m, 2 H, *o*-H, PhP), 7.38 (d, 4 H, *o*-H, Ph, $^3J_{HH}$ = 8.7 Hz), 7.21 (m, 3 H, *p*-, *m*-H, PhP), 6.74 (d, 4 H, *m*-H, Ph, $^3J_{HH}$ = 8.7 Hz), 4.35 (d, 2 H, PCH$_2$, $^2J_{PH}$ = 17.4 Hz), 3.68 (s, 6 H, OCH$_3$), 1.76 (d, 6 H, PCH$_3$, $^2J_{PH}$ = 13.1 Hz). − ^{13}C NMR (90.6 MHz, 243 K, [D$_8$]THF): δ = 158.4 (*p*-C, Ph), 151.8 (d, *i*-C, PhP, $^1J_{PC}$ = 47.2 Hz), 144.4 (d, *i*-C, Ph, $^3J_{PC}$ = 6.9 Hz), 129.5 (d, *o*-C, PhP, $^2J_{PC}$ = 6.9 Hz), 128.4 (d, *m*-C, PhP, $^3J_{PC}$ = 8.3 Hz), 128.1 (s, *p*-C, PhP, $^4J_{PC}$ = 0 Hz), 127.4 (*o*-C, Ph), 113.3 (*m*-C, Ph), 69.6 (d, C-4, $^2J_{PC}$ = 13.9 Hz), 67.1 (d, C-3, $^1J_{PC}$ = 88.8 Hz), 55.1 (OCH$_3$), 22.6 (d, PCH$_3$, $^1J_{PC}$ = 84.6 Hz). − ^{31}P NMR (81.0 MHz, 243 K, [D$_8$]THF): δ = −84.8.

***P,P,P*-Trimethyl-4,4-diphenyl-1,2-oxaphosphetane (3′d):** 8 mg (89 μmol) of trimethyl(methylene)phosphorane was treated with 16 mg (88 μmol) of benzophenone in ca. 0.6 mL of [D$_8$]THF at −78°C. − ^{1}H NMR (599.9 MHz, 203 K, [D$_8$]THF): δ = 7.56 (m, 4 H, *o*-H, Ph), 7.20 (m, 4 H, *m*-H, Ph), 7.04 (m, 2 H, *p*-H, Ph), 4.31 (d, 2 H, PCH$_2$, $^2J_{PH}$ = 16.5 Hz), 1.26 (d, 9 H, PCH$_3$, $^2J_{PH}$ = 11.7 Hz). − ^{13}C NMR (150.8 MHz, 203 K, [D$_8$]THF): δ = 152.8 (d, *i*-C, Ph, $^3J_{PC}$ = 8.2 Hz), 128.2 (*m*-C, Ph), 126.4 (*o*-C, Ph), 125.9 (*p*-C, Ph), 79.7 (d, C-4, $^2J_{PC}$ = 13.9 Hz), 65.3 (d, C-3, $^1J_{PC}$ = 88.5 Hz), 24.1 (d, PCH$_3$, $^1J_{PC}$ = 68.3 Hz). − ^{31}P NMR (242.9 MHz, 203 K, [D$_8$]THF): δ = −88.2.

***P*-Cyclopropyl-*P,P*,4,4-tetraphenyl-1,2-oxaphosphetane (3′e):** 26 mg (108 μmol) of (cyclopropyl)(methylene)diphenylphosphorane was treated with 20 mg (110 μmol) of benzophenone in 700 mg of [D$_8$]THF at −78°C. − ^{1}H NMR (360.1 MHz, 243 K, [D$_8$]THF): δ = 7.39 (m, 4 H, *o*-H, Ph), 7.25 (m, 4 H, *o*-H, Ph$_2$P), 7.15 (m, 6 H, *m*-, *p*-H, Ph$_2$P), 7.13 (m, 4 H, *m*-H, Ph), 7.03 (m, 2 H, *p*-H, Ph), 4.80 (d, 2 H, PCH$_2$, $^2J_{PH}$ = 16.8 Hz), 1.23 (br. m, 2 H, CH$_2$), 0.89 (m, 1 H, PCH), 0.82 (m, 2 H, CH$_2$). − ^{13}C NMR (90.6 MHz, 243 K, [D$_8$]THF): δ = 151.1 (d, *i*-C, Ph, $^3J_{PC}$ = 6.9 Hz), 147.8 (d, *i*-C, Ph$_2$P, $^1J_{PC}$ = 70.8 Hz), 130.7 (d, *o*-C, Ph$_2$P, $^2J_{PC}$ = 8.3 Hz), 128.4 (*m*-C, Ph), 128.3 (s, *p*-C, Ph$_2$P, $^4J_{PC}$ = 0 Hz), 128.1 (d, *m*-C, Ph$_2$P, $^3J_{PC}$ = 11.1 Hz), 126.3 (*p*-C and *o*-C, Ph), 70.4 (d, C-4, $^2J_{PC}$ = 13.9 Hz), 64.6 (d, C-3, $^1J_{PC}$ = 90.2 Hz), 13.4 (d, PCH, $^1J_{PC}$ = 142.9 Hz), 5.7 (d, CH$_2$, $^2J_{PC}$ = 4.2 Hz). − ^{31}P NMR (81.0 MHz, 243 K, [D$_8$]THF): δ = −66.7.

***P,P*-Dicyclopropyl-*P*,4,4-triphenyl-1,2-oxaphosphetane (3′f):** 31 mg (151 μmol) of dicyclopropyl(methylene)(phenyl)phosphorane was treated with 28 mg (154 μmol) of benzophenone in 700 mg of [D$_8$]THF at −78°C. − ^{1}H NMR (360.1 MHz, 243 K, [D$_8$]THF): δ = 7.63 (m, 2 H, *m*-H, PhP), 7.38 (m, 4 H, *o*-H, Ph), 7.23 (m, 2 H, *o*-H, PhP), 7.16 (m, 5 H, *m*-H, Ph and *p*-H, PhP), 7.04 (m, 2 H, *p*-H, Ph), 4.19 (d, 2 H, PCH$_2$, $^2J_{PH}$ = 16.9 Hz), 1.30 (m, 2 H, PCH), 1.00, 0.73 (m, each 2 H, CH$_2$), 0.62 (m, 4 H, CH$_2$). − ^{13}C NMR (90.6 MHz, 243 K, [D$_8$]THF): δ = 154.0 (d, *i*-C, PhP, $^1J_{PC}$ = 32.3 Hz), 151.3 (d, *i*-C, Ph, $^3J_{PC}$ = 6.9 Hz), 129.8 (d, *o*-C, PhP, $^2J_{PC}$ = 5.6 Hz), 128.5 (*m*-C, Ph), 128.2 (d, *m*-C, PhP, $^3J_{PC}$ = 5.6 Hz), 127.5 (s, *p*-C, PhP, $^4J_{PC}$ = 0 Hz), 126.3 (*p*-C, Ph), 126.1 (*o*-C, Ph), 70.2 (d, C-4, $^2J_{PC}$ = 12.5 Hz), 66.6 (d, C-3, $^1J_{PC}$ = 97.1 Hz), 12.9 (d, PCH, $^1J_{PC}$ = 129.0 Hz), 5.0 (d, CH$_2$, $^2J_{PC}$ = 5.6 Hz), 4.1 (d, CH$_2$, $^2J_{PC}$ = 2.8 Hz). − ^{31}P NMR (81.0 MHz, 243 K, [D$_8$]THF): δ = −70.1.

***P,P,P*-Tricyclopropyl-4,4-bis(4′-methoxyphenyl)-1,2-oxaphosphetane (3g):** 14 mg (83 μmol) of tricyclopropyl(methylene)phosphorane was treated with 19 mg (78 μmol) of 4,4′-dimethoxybenzophenone in ca. 0.6 mL of [D$_8$]THF at −78°C. − ^{1}H NMR (360.1 MHz, 243 K, [D$_8$]THF): δ = 7.26 (d, 4 H, *o*-H, Ph, $^3J_{HH}$ = 8.7 Hz), 6.70 (d, 4 H, *m*-H, Ph, $^3J_{HH}$ = 8.7 Hz), 4.18 (d, 2 H, PCH$_2$, $^2J_{PH}$ = 16.5 Hz), 3.67 (s, 6 H, OCH$_3$), 0.71 (m, 6 H, CH$_2$), 0.58 (m, 3 H, PCH), 0.46 (m, 6 H, CH$_2$). − ^{13}C NMR (90.6 MHz, 243 K, [D$_8$]THF): δ = 158.2 (*p*-C, Ph), 144.3 (d, *i*-C, Ph, $^3J_{PC}$ = 6.9 Hz), 127.0 (*o*-C, Ph), 113.4 (*m*-C, Ph), 69.5 (d, C-4, $^2J_{PC}$ =

12.5 Hz), 59.3 (d, C-3, $^1J_{PC}$ = 94.3 Hz), 55.0 (OCH_3), 13.2 (d, PCH, $^1J_{PC}$ = 97.1 Hz), 4.1 (d, CH_2, $^2J_{PC}$ = 2.8 Hz). − ^{31}P NMR (81.0 MHz, 243 K, [D$_8$]THF): δ = −68.5.

(±)-*P*-Ethyl-4,4-bis(4′-methoxyphenyl)-3-methyl-*P*,*P*-diphenyl-1,2-oxaphosphetane (3h): 33 mg (136 μmol) of (ethyl)(ethylidene)diphenylphosphorane was treated with 35 mg (135 μmol) of 4,4′-dimethoxybenzophenone in 870 mg of [D$_8$]THF at −78°C. − ^{1}H NMR (200.1 MHz, 243 K, [D$_8$]THF): δ = 7.51−7.17 (m, 10 H, *o*-, *m*-, *p*-H, PPh_2), 7.45 (d, 2 H, *o*-H, Ph, $^3J_{HH}$ = 8.7 Hz), 7.10 (d, 2 H, *o*-H′, Ph, $^3J_{HH}$ = 8.7 Hz), 6.85 (d, 2 H, *m*-H, Ph, $^3J_{HH}$ = 8.7 Hz), 6.58 (d, 2 H, *m*-H′, Ph, $^3J_{HH}$ = 8.7 Hz), 5.21 (dq, 1 H, PC*H*CH_3, $^2J_{PH}$ = 18.6 Hz, $^3J_{HH}$ = 8.3 Hz), 3.75, 3.63 (s, each 3 H, OCH_3, OCH_3′), 2.58, 2.18 (m, each 1 H, PCHH′), 1.17−0.94 (m, 6 H, PCHCH_3 and PCH_2CH_3 signals superimposed). − ^{13}C NMR (50.3 MHz, 243 K, [D$_8$]THF): δ = 158.7 (*p*-C, Ph), 158.4 (*p*-C′, Ph), 148.5 (d, *i*-C, Ph_2P, $^1J_{PC}$ = 47.3 Hz), 144.6 (d, *i*-C, Ph, $^3J_{PC}$ = 9.5 Hz), 143.5 (d, *i*-C′, Ph_2P, $^1J_{PC}$ = 88.5 Hz), 139.5 (d, *i*-C′, Ph, $^3J_{PC}$ = 5.2 Hz), 133.5 (d, *o*-C, Ph_2P, $^2J_{PC}$ = 7.0 Hz), 132.8 (d, *o*-C′, Ph_2P, $^2J_{PC}$ = 7.3 Hz), 129.33 (d, *p*-C, Ph_2P, $^4J_{PC}$ = 1.8 Hz), 129.25 (d, *p*-C′, Ph_2P, $^4J_{PC}$ = 1.8 Hz), 128.8 (*o*-C, Ph), 128.2 (d, *m*-C, Ph_2P, $^3J_{PC}$ = 10.7 Hz), 128.1 (*o*-C′, Ph), 127.9 (d, *m*-C′, Ph_2P, $^3J_{PC}$ = 8.5 Hz), 113.4 (*m*-C, Ph), 112.9 (*m*-C′, Ph), 74.3 (d, C-4, $^2J_{PC}$ = 12.2 Hz), 68.4 (d, C-3, $^1J_{PC}$ = 91.3 Hz), 55.1 (OCH_3), 55.0 (OCH_3′), 29.5 (d, P*C*H_2CH_3, $^1J_{PC}$ = 95.5 Hz), 14.3 (d, PCH*C*H_3, $^2J_{PC}$ = 7.6 Hz), 8.4 (d, PCH_2CH_3, $^2J_{PC}$ = 5.8 Hz). − ^{31}P NMR (81.0 MHz, 243 K, [D$_8$]THF): δ = −62.8.

(±)-*P*,*P*-Diethyl-4,4-bis(4′-methoxyphenyl)-3-methyl-*P*-phenyl-1,2-oxaphosphetane (3i): 16 mg (82 μmol) of diethyl(ethylidene)(phenyl)-phosphorane was treated with 20 mg (83 μmol) of 4,4′-dimethoxybenzophenone in ca. 0.6 mL of [D$_8$]THF at −78°C. − ^{1}H NMR (360.1 MHz, 263 K, [D$_8$]THF): δ = 7.41 (d, 2 H, *o*-H, Ph, $^3J_{HH}$ = 8.7 Hz), 7.37 (m, 2 H, *o*-H, PhP), 7.30 (d, 2 H, *o*-H′, Ph, $^3J_{HH}$ = 8.7 Hz), 7.24 (m, 2 H, *m*-H, PhP), 7.20 (m, 1 H, *p*-H, PhP), 6.79 (d, 2 H, *m*-H, Ph, $^3J_{HH}$ = 8.7 Hz), 6.68 (d, 2 H, *m*-H′, Ph, $^3J_{HH}$ = 8.7 Hz), 4.73 (m, 1 H, PC*H*CH_3, $^2J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 7.8 Hz), 3.73, 3.66 (s, each 3 H, OCH_3, OCH_3′), 2.38, 2.27, 2.09, 1.99 (m, each 1 H, PCHH′), 1.33 (dt, 3 H, PCHCH_3, $^3J_{PH}$ = 19.4 Hz, $^3J_{HH}$ = 7.8 Hz), 0.90 (dt, 3 H, PCH_2CH_3, $^3J_{PH}$ = 18.9 Hz, $^3J_{HH}$ = 7.8 Hz), 0.90 (dd, 3 H, PCHCH_3, $^3J_{PH}$ = 26.6 Hz, $^3J_{HH}$ = 7.8 Hz). − ^{13}C NMR (90.6 MHz, 263 K, [D$_8$]THF): δ = 158.5 (*p*-C, Ph), 158.4 (*p*-C′, Ph), 149.2 (d, *i*-C, PhP, $^1J_{PC}$ = 23.6 Hz), 145.4 (d, *i*-C, Ph, $^3J_{PC}$ = 6.9 Hz), 140.2 (d, *i*-C′, Ph, $^3J_{PC}$ = 5.6 Hz), 131.1 (d, *p*-C, PhP, $^4J_{PC}$ = 4.2 Hz), 128.6 (*o*-C, Ph), 128.4 (d, *o*-C, PhP, $^2J_{PC}$ = 6.9 Hz), 128.35 (*o*-C′, Ph), 127.8 (d, *m*-C, PhP, $^3J_{PC}$ = 6.9 Hz), 113.3 (*m*-C, Ph), 113.0 (*m*-C′, Ph), 73.5 (d, C-4, $^2J_{PC}$ = 12.5 Hz), 68.7 (d, C-3, $^1J_{PC}$ = 94.3 Hz), 55.1 (OCH_3), 55.0 (OCH_3′), 27.6 (d, PCH_2, $^1J_{PC}$ = 83.2 Hz), 23.7 (d, PCH_2, $^1J_{PC}$ = 87.4 Hz), 13.9 (d, PCH*C*H_3, $^2J_{PC}$ = 6.9 Hz), 9.3 (d, PCH_2CH_3, $^2J_{PC}$ = 4.9 Hz), 9.2 (d, $PCH_2C'H_3$, $^2J_{PC}$ = 5.6 Hz). − ^{31}P NMR (81.0 MHz, 243 K, [D$_8$]THF): δ = −64.8.

(±)-*P*,*P*,*P*-Triethyl-4,4-bis(4′-methoxyphenyl)-3-methyl-1,2-oxaphosphetane (3k): 19 mg (130 μmol) of triethyl(ethylidene)phosphorane was treated with 33 mg (136 μmol) of 4,4′-dimethoxybenzophenone in ca. 0.8 mL of [D$_8$]THF at −78°C. − ^{1}H NMR (360.1 MHz, 243 K, [D$_8$]THF): δ = 7.37 (d, 2 × 2 H, *o*-H, *o*-H′, Ph, $^3J_{HH}$ = 8.4 Hz), 6.75 (d, 2 H, *m*-H, Ph, $^3J_{HH}$ = 8.4 Hz), 6.71 (d, 2 H, *m*-H′, Ph, $^3J_{HH}$ = 8.4 Hz), 4.62 (m, 1 H, PC*H*CH_3, $^2J_{PH}$ = 15.8 Hz, $^3J_{HH}$ = 7.9 Hz), 3.71, 3.68 (s, each 3 H, OCH_3, OCH_3′), 1.58 (m, 6 H, PCH_2), 1.24 (dd, 3 H, PCHCH_3, $^3J_{PH}$ = 24.5 Hz, $^3J_{HH}$ = 7.9 Hz), 1.12 (dt, 9 H, PCH_2CH_3, $^3J_{PH}$ = 16.3 Hz, $^3J_{HH}$ = 8.7 Hz). − ^{13}C NMR (90.6 MHz, 243 K, [D$_8$]THF): δ = 158.3 (*p*-C and *p*-C′, Ph), 145.9 (d, *i*-C, Ph, $^3J_{PC}$ = 6.9 Hz), 140.8 (d, *i*-C′, Ph, $^3J_{PC}$ = 6.4 Hz), 128.6 (*o*-C, Ph), 127.8 (*o*-C′, Ph), 113.1 (*m*-C, Ph), 112.9 (*m*-C′, Ph), 72.7 (d, C-4, $^2J_{PC}$ = 11.6 Hz), 63.9 (d, C-3, $^1J_{PC}$ = 90.4 Hz), 55.0 (OCH_3, OCH_3′), 26.1 (d, PCH_2, $^1J_{PC}$ = 63.1 Hz), 14.0 (d, PCH*C*H_3, $^2J_{PC}$ = 6.6 Hz), 9.3 (d, PCH_2CH_3, $^2J_{PC}$ = 4.6 Hz). − ^{31}P NMR (81.0 MHz, 243 K, [D$_8$]THF): δ = −65.5.

Generation of the Thiabetaine 5a: 18 mg (65 μmol) of (methylene)-triphenylphosphorane was treated with 16 mg (62 μmol) of 4,4′-dimethoxythiobenzophenone in 1.1 g of [D$_2$]dichloromethane at −78°C. − ^{1}H NMR (360.1 MHz, 243 K, [D$_2$]dichloromethane): δ = 7.66 (m, 6 H, *o*-H, Ph_3P), 7.46 (m, 6 H, *p*-H, Ph_3P), 7.40 (d, 4 H, *o*-H, Ph, $^3J_{HH}$ = 8.5 Hz), 7.33 (m, 6 H, *m*-H, Ph_3P), 6.53 (d, 4 H, *m*-H, Ph, $^3J_{HH}$ = 8.5 Hz), 5.18 (d, 2 H, PCH_2, $^2J_{PH}$ = 9.8 Hz), 3.68 (s, 6 H, OCH_3). − ^{13}C NMR (90.6 MHz, 243 K, [D$_2$]dichloromethane): δ = 156.2 (*p*-C, Ph), 144.0 (d, *i*-C, Ph, $^3J_{PC}$ = 7.4 Hz), 133.5 (d, *o*-C, Ph_3P, $^2J_{PC}$ = 8.4 Hz), 131.4 (d, *p*-C, Ph_3P, $^4J_{PC}$ = 3.2 Hz), 128.08 (*o*-C, Ph), 128.10 (d, *m*-C, Ph_3P, $^3J_{PC}$ = 11.6 Hz), 126.6 (d, *i*-C, Ph_3P, $^1J_{PC}$ = 91.6 Hz), 111.9 (*m*-C, Ph), 55.0 (OCH_3), 51.8 (d, C-3, $^1J_{PC}$ = 82.1 Hz), 49.7 (d, C-4, $^2J_{PC}$ = 2.1 Hz). − ^{31}P NMR (81.0 MHz, 223 K, [D$_2$]dichloromethane): δ = +3.6; (243 K): δ = +0.4.

Thiabetaine 5b: 31 mg (145 μmol) of (methyl)(methylene)diphenylphosphorane was treated with 37 mg (143 μmol) of 4,4′-dimethoxythiobenzophenone in 720 mg of [D$_5$]pyridine at −35°C. − ^{1}H NMR (200.1 MHz, 263 K, [D$_5$]pyridine): δ = 8.28 (d, 4 H, *o*-H, Ph, $^3J_{HH}$ = 8.7 Hz), 7.82 (m, 4 H, *o*-H, Ph_2P), 7.39 (m, 6 H, m, *p*-H, Ph_2P), 6.91 (d, 4 H, *m*-H, Ph, $^3J_{HH}$ = 8.7 Hz), 5.01 (d, 2 H, PCH_2, $^2J_{PH}$ = 10.0 Hz), 3.59 (s, 6 H, OCH_3), 2.83 (d, 3 H, PCH_3, $^2J_{PH}$ = 14.3 Hz). − ^{13}C NMR (50.3 MHz, 263 K, [D$_5$]pyridine): δ = 157.4 (*p*-C, Ph), 146.8 (d, *i*-C, Ph, $^3J_{PC}$ = 8.3 Hz), 132.3 (d, *o*-C, Ph_2P, $^2J_{PC}$ = 9.1 Hz), 131.9 (d, *p*-C, Ph_2P, $^4J_{PC}$ = 2.5 Hz), 129.8 (d, *i*-C, Ph_2P, $^1J_{PC}$ = 85.8 Hz), 129.7 (*o*-C, Ph), 129.2 (d, *m*-C, Ph_2P, $^3J_{PC}$ = 12.0 Hz), 112.9 (*m*-C, Ph), 55.1 (OCH_3), 51.9 (d, C-4, $^2J_{PC}$ = 2.5 Hz), 51.6 (d, C-3, $^1J_{PC}$ = 78.8 Hz), 14.2 (d, PCH_3, $^1J_{PC}$ = 64.3 Hz). − ^{31}P NMR (81.0 MHz, 243 K, [D$_5$]pyridine): δ = +4.4; (263 K): δ = +1.9.

Thiabetaine 5c: 13 mg (85 μmol) of dimethyl(methylene)(phenyl)phosphorane was treated with 23 mg (89 μmol) of 4,4′-dimethoxythiobenzophenone in 880 mg of [D$_5$]pyridine at −35°C. − ^{1}H NMR (599.9 MHz, 293 K, [D$_5$]pyridine): δ = 8.23 (d, 4 H, *o*-H, Ph, $^3J_{HH}$ = 8.8 Hz), 7.86 (m, 2 H, *o*-H, PhP), 7.52 (m, 1 H, *p*-H, PhP), 7.47 (m, 2 H, *m*-H, PhP), 6.89 (d, 4 H, *m*-H, Ph, $^3J_{HH}$ = 8.8 Hz), 4.37 (d, 2 H, PCH_2, $^2J_{PH}$ = 10.6 Hz), 3.57 (s, 6 H, OCH_3), 2.40 (d, 6 H, PCH_3, $^2J_{PH}$ = 14.1 Hz). − ^{13}C NMR (150.8 MHz, 293 K, [D$_5$]pyridine): δ = 157.4 (*p*-C, Ph), 147.2 (d, *i*-C, Ph, $^3J_{PC}$ = 8.9 Hz), 132.3 (d, *p*-C, PhP, $^4J_{PC}$ = 2.7 Hz), 131.2 (d, *o*-C, PhP, $^2J_{PC}$ = 8.9 Hz), 129.7 (*o*-C, Ph), 129.5 (d, *m*-C, PhP, $^3J_{PC}$ = 11.6 Hz), 129.2 (d, *i*-C, PhP, $^1J_{PC}$ = 82.1 Hz), 112.8 (*m*-C, Ph), 55.1 (OCH_3), 52.2 (d, C-4, $^2J_{PC}$ = 2.7 Hz), 50.9 (d, C-3, $^1J_{PC}$ = 73.9 Hz), 14.1 (d, PCH_3, $^1J_{PC}$ = 60.6 Hz). − ^{31}P NMR (242.9 MHz, 253 K, [D$_5$]pyridine): δ = +14.5; (273 K): δ = +12.0; (293 K): δ = +9.2.

Thiabetaine 5d: 25 μL of methanol (abs.) in 5 mL of THF was added to 98 mg (0.60 mmol) of Me_3P=CHTMS in 10 mL of THF at room temperature. Then the mixture was stirred at 0°C for 20 min. To this mixture a solution of 156 mg (0.60 mmol) of bis(*p*-methoxyphenyl) thioketone (i.e. 4,4′-dimethoxythiobenzophenone) in 2 mL of THF was added until the color of the slurry remained pale blue. The precipitate was collected and dried in vacuo to give 153 mg (73%) of the betaine. − ^{1}H NMR (200.1 MHz, 300 K, [D$_5$]pyridine): δ = 8.25 (d, 4 H, *o*-H, Ph, $^3J_{HH}$ = 8.9 Hz), 6.91 (d, 4 H, *m*-H, Ph, $^3J_{HH}$ = 8.9 Hz), 4.05 (d, 2 H, PCH_2, $^2J_{PH}$ = 10.5 Hz), 3.63 (s, 6 H, OCH_3), 1.98 (d, 9 H, PCH_3, $^2J_{PH}$ =

13.8 Hz). – ^{13}C NMR (50.3 MHz, 300 K, [D$_5$]pyridine): δ = 157.4 (*p*-C, Ph), 147.5 (d, *i*-C, Ph, $^3J_{PC}$ = 8.3 Hz), 129.7 (*o*-C, Ph), 112.8 (*m*-C, Ph), 55.1 (OCH_3), 51.9 (d, C-4, $^2J_{PC}$ = 3.3 Hz), 49.1 (d, C-3, $^1J_{PC}$ = 75.1 Hz), 14.3 (d, PCH_3, $^1J_{PC}$ = 59.4 Hz). – ^{31}P NMR (81.0 MHz, 300 K, [D$_5$]pyridine): δ = +11.5. – $C_{19}H_{25}PSO_2$ (348.45): calcd. C 65.49, H 7.23; found C 65.22, H 7.09. – M.p. 79°C (dec.). – IR: $\tilde{\nu}$ = 3052, 2960, 2894, 2835, 1604, 1506, 1467, 1290. 1249, 1183, 1111, 1045, 959, 907, 827 cm^{-1}.

Thiabetaine 5e: 31 mg (129 μmol) of (cyclopropyl)(methylene)diphenylphosphorane was treated with 33 mg (128 μmol) of 4,4′-dimethoxythiobenzophenone in 720 mg of [D$_5$]pyridine at −35°C. – ^{1}H NMR (360.1 MHz, 263 K, [D$_5$]pyridine): δ = 8.32 (d, 4 H, *o*-H, Ph, $^3J_{HH}$ = 8.9 Hz), 7.64 (m, 4 H, *o*-H, Ph_2P), 7.47 (m, 2 H, *p*-H, Ph_2P), 7.37 (m, 4 H, *m*-H, Ph_2P), 6.88 (d, 4 H, *m*-H, Ph, $^3J_{HH}$ = 8.9 Hz), 5.16 (d, 2 H, PCH_2, $^2J_{PH}$ = 10.0 Hz), 3.57 (s, 6 H, OCH_3), 3.47 (m, 1 H, PCH), 0.59 (m, 2 H, CH_2), 0.11 (m, 2 H, CH_2). – ^{13}C NMR (90.6 MHz, 263 K, [D$_5$]pyridine): δ = 157.2 (*p*-C, Ph), 147.0 (d, *i*-C, Ph, $^3J_{PC}$ = 8.4 Hz), 133.4 (d, *o*-C, Ph_2P, $^2J_{PC}$ = 8.4 Hz), 132.0 (d, *p*-C, Ph_2P, $^4J_{PC}$ = 2.1 Hz), 129.7 (*o*-C, Ph), 129.0 (d, *m*-C, Ph_2P, $^3J_{PC}$ = 11.6 Hz), 127.3 (d, *i*-C, Ph_2P, $^1J_{PC}$ = 86.3 Hz), 112.7 (*m*-C, Ph), 55.1 (OCH_3), 52.1 (d, C-3, $^1J_{PC}$ = 77.9 Hz), 51.9 (d, C-4, $^2J_{PC}$ = 2.1 Hz), 6.0 (d, PCH, $^1J_{PC}$ = 94.7 Hz), 4.2 (d, CH_2, $^2J_{PC}$ = 4.2 Hz). – ^{31}P NMR (81.0 MHz, 243 K, [D$_5$]pyridine): δ = +16.9; (263 K): δ = +13.9; (283 K): δ = +10.5.

Thiabetaine 5f: 21 mg (103 μmol) of dicyclopropyl(methylene)-(phenyl)phosphorane was treated with 23 mg (89 μmol) of 4,4′-dimethoxythiobenzophenone in ca. 0.6 mL of [D$_5$]pyridine at −35°C. – ^{1}H NMR (360.1 MHz, 283 K, [D$_5$]pyridine): δ = 8.28 (d, 4 H, *o*-H, Ph, $^3J_{HH}$ = 8.8 Hz), 8.02 (m, 2 H, *o*-H, PhP), 7.41 (m, 3 H, *m*-, *p*-H, PhP), 6.91 (d, 4 H, *m*-H, Ph, $^3J_{HH}$ = 8.8 Hz), 4.59 (d, 2 H, PCH_2, $^2J_{PH}$ = 9.9 Hz), 3.62 (s, 6 H, OCH_3), 1.97 (m, 2 H, PCH), 0.90, 0.83, 0.66, 0.55 (m, each 2 H, CH_2). – ^{13}C NMR (90.6 MHz, 283 K, [D$_5$]pyridine): δ = 157.3 (*p*-C, Ph), 147.3 (d, *i*-C, Ph, $^3J_{PC}$ = 8.2 Hz), 131.5 (d, *o*-C, PhP, $^2J_{PC}$ = 8.2 Hz), 131.2 (d, *p*-C, PhP, $^4J_{PC}$ = 2.7 Hz), 129.8 (*o*-C, Ph), 128.7 (d, *m*-C, PhP, $^3J_{PC}$ = 13.6 Hz), 128.5 (d, *i*-C, PhP, $^1J_{PC}$ = 101.4 Hz), 112.7 (*m*-C, Ph), 55.1 (OCH_3), 51.9 (d, C-4, $^2J_{PC}$ = 2.2 Hz), 48.8 (d, C-3, $^1J_{PC}$ = 81.2 Hz), 4.5 (d, CH_2, $^2J_{PC}$ = 4.9 Hz), 4.0 (d, CH_2, $^2J_{PC}$ = 4.9 Hz), 3.7 (d, PCH, $^1J_{PC}$ = 85.0 Hz). – ^{31}P NMR (81.0 MHz, 243 K, [D$_5$]pyridine): δ = + 20.0; (263 K): δ = + 18.6; (283 K): δ = + 16.8. – GHSQC NMR (150.8/599.9 MHz, 283 K, [D$_5$]pyridine): δ = 131.5/8.02 (*o*-C, PhP/*o*-H, PhP), 131.2/7.41 (*p*-C, PhP/*p*-H, PhP), 129.8/8.28 (*o*-C, Ph/*o*-H, Ph), 128.7/7.41 (*m*-C, PhP/*m*-H, PPh), 112.7/6.91 (*m*-C, Ph/*m*-H, PPh), 55.1/3.62 (OCH_3), 48.8/4.59 (C-3/PCH_2), 4.5/0.90 (CH_2/CH_2), 4.5/0.55 (CH_2/CH_2), 4.0/0.83 (CH_2/CH_2), 4.0/0.66 (CH_2/CH_2), 3.7/1.97 (PCH/PCH). – GHMBC NMR (150.8/599.9 MHz, 283 K, [D$_5$]pyridine): δ = 157.3/8.28 (*p*-C, Ph/*o*-H, Ph), 157.3/6.91 (*p*-C, Ph/*m*-H, Ph), 157.3/3.62 (*p*-C, Ph/OCH_3), 147.3/8.28 (*i*-C, Ph/*o*-H, Ph), 147.3/6.91 (*i*-C, Ph/*m*-H, Ph), 147.3/4.59 (*i*-C, Ph/PCH_2), 131.5/7.41 (*o*-C, PhP/*p*-H, PPh), 131.2/8.02 (*p*-C, PhP/*o*-H, PhP), 129.8/6.91 (*o*-C, Ph/*m*-H, Ph), 128.5/7.41 (*i*-C, PhP/*m*-H, Ph), 128.5/4.59 (*i*-C, PhP/CH_2), 112.7/8.28 (*m*-C, Ph/*o*-H, Ph), 51.9/8.28 (C-4/*o*-H, Ph), 51.9/4.59 (C-4/PCH_2), 4.0/1.97 (CH_2/PCH), 3.7/0.90, 0.83, 0.66, 0.55 (PCH/CH_2).

Thiabetaine (5g): 19 mg (113 μmol) of tricyclopropyl(methylene)-phosphorane was treated with 29 mg (112 μmol) of 4,4′-dimethoxythiobenzophenone in ca. 0.6 mL of [D$_5$]pyridine at −35°C. – ^{1}H NMR (599.9 MHz, 300 K, [D$_5$]pyridine): δ = 8.26 (d, 4 H, *o*-H, $^3J_{HH}$ = 8.9 Hz), 6.91 (d, 4 H, *m*-H, $^3J_{HH}$ = 8.9 Hz), 3.89 (d, 2 H, PCH_2, $^2J_{PH}$ = 10.6 Hz), 3.65 (s, 6 H, OCH_3), 1.91 (m, 3 H, PCH), 1.01 (m, 6 H, CH_2), 0.77 (m, 6 H, CH_2). – ^{13}C NMR (150.8 MHz, 300 K, [D$_5$]pyridine): δ = 157.3 (*p*-C, Ph), 147.6 (d, *i*-C, Ph, $^3J_{PC}$ = 9.1 Hz), 129.9 (*o*-C, Ph), 112.7 (*m*-C, Ph), 55.2 (OCH_3), 51.1 (d, C-4, $^2J_{PC}$ = 1.9 Hz), 46.0 (d, C-3, $^1J_{PC}$ = 71.7 Hz), 4.3 (d, CH_2, $^2J_{PC}$ = 4.6 Hz), 3.6 (d, CH, $^1J_{PC}$ = 87.9 Hz). – ^{31}P NMR (242.9 MHz, 243 K, [D$_5$]pyridine): δ = +33.5; (263 K): δ = +32.2; (300 K): δ = +29.9.

Thiabetaine 11: 12 mg (71 μmol) of tricyclopropyl(methylene)phosphorane was treated with 20 mg (70 μmol) of 4,4′-bis(dimethylamino)thiobenzophenone in 890 mg of [D$_5$]pyridine at −35°C. After the measurement, crystal growth set in. Single crystals suited for the X-ray crystal-structure analysis were obtained after keeping the sample at +4°C overnight. – ^{1}H NMR (599.9 MHz, 300 K, [D$_5$]pyridine): δ = 8.22 (d, 4 H, *o*-H, $^3J_{HH}$ = 9.0 Hz), 6.74 (d, 4 H, *m*-H, $^3J_{HH}$ = 9.0 Hz), 3.89 (d, 2 H, PCH_2, $^2J_{PH}$ = 10.2 Hz), 2.75 [s, 12 H, $N(CH_3)_2$], 1.92 (m, 3 H, PCH), 1.00 (m, 6 H, CH_2), 0.75 (m, 6 H, CH_2). – ^{13}C NMR (150.8 MHz, 300 K, [D$_5$]pyridine): δ = 148.4 (*p*-C, Ph), 144.1 (d, *i*-C, Ph, $^3J_{PC}$ = 8.6 Hz), 129.5 (*o*-C, Ph), 112.2 (*m*-C, Ph), 50.8 (d, C-4, $^2J_{PC}$ = 1.8 Hz), 46.4 (d, C-3, $^1J_{PC}$ = 72.2 Hz), 40.9 $[N(CH_3)_2]$, 4.2 (d, CH_2, $^2J_{PC}$ = 4.8 Hz), 4.0 (d, CH, $^1J_{PC}$ = 87.8 Hz). – ^{31}P NMR (242.9 MHz, 263 K, [D$_5$]pyridine): δ = +30.4; (283 K): δ = +29.0; (300 K): δ = +27.7.

X-ray Crystal-Structure Analysis of 11: Empirical formula $C_{27}H_{37}N_2PS \cdot C_5H_5N$, M = 531.72, yellow crystal, 0.40 × 0.20 × 0.10 mm, a = 9.814(1), b = 24.299(3), c = 12.633(1) Å, β = 97.56(1)°, V = 2986.4(5) Å^3, $\rho_{calcd.}$ = 1.183 g cm^{-3}, F(000) = 1144 e, μ = 16.44 cm^{-1}, empirical absorption correction with φ scan data (0.914 ≤ C ≤ 0.999), Z = 4, monoclinic, space group $P2_1/n$ (no. 14), λ = 1.54178 Å, T = 223 K, ω/2θ scans, 6359 reflections collected (±h, +k, +l), (sinθ)/λ = 0.62 Å^{-1}, 6085 independent and 4063 observed reflections [$I \geq 2\ \sigma(I)$], 326 refined parameters, R = 0.078, wR^2 = 0.232, max. residual electron density 10.2 (−0.74) eÅ^{-3}, disordered pyridine molecule (refined with restraints as rigid six-membered ring, highest positive and negative Fourier peaks in the solvent molecule area), hydrogen atoms calculated and refined as riding atoms. Data set was collected with an Enraf Nonius CAD4 diffractometer. Programs used: data reduction MolEN, structure solution SHELXS-86, structure refinement SHELXL-97, graphics SCHAKAL-92. Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-115321. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, CambridgeCB2 1EZ, UK [Fax: int. code + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

(±)-Thiabetaine 5h: 15 mg (62 μmol) of (ethyl)(ethylidene)diphenylphosphorane was treated with 15 mg (58 μmol) of 4,4′-dimethoxythiobenzophenone in 850 mg of [D$_5$]pyridine at −35°C. – ^{1}H NMR (360.1 MHz, 263 K, [D$_5$]pyridine): δ = 8.65 (d, 2 H, *o*-H, Ph, $^3J_{HH}$ = 8.8 Hz), 8.33 (d, 2 H, *o*-H′, Ph, $^3J_{HH}$ = 8.8 Hz), 8.26 (m, 2 H, *o*-H, PPh_2), 7.82 (m, 2 H, *o*-H′, PPh_2), 7.55−7.28 (m, 2 H, *p*-H, *p*-H′, PPh_2), 7.35 (m, 4 H, *m*-H, *m*-H′, PPh_2), 6.95 (d, 2 H, *m*-H, Ph, $^3J_{HH}$ = 8.8 Hz), 6.85 (d, 2 H, *m*-H′, Ph, $^3J_{HH}$ = 8.8 Hz), 5.50 (q, 1 H, PC*H*CH_3, $^2J_{PH}$ = 0 Hz, $^3J_{HH}$ = 6.6 Hz), 4.06 (m, 1 H, PCHH′), 3.56, 3.49 (s, each 3 H, OCH_3, OCH_3′), 2.86 (m, 1 H, PCHH′), 1.68 (dd, 3 H, PCHC*H*$_3$, $^2J_{PH}$ = 20.4 Hz, $^3J_{HH}$ = 6.6 Hz), 0.57 (dt, 3 H, PCH_2CH_3 $^2J_{PH}$ = 20.9 Hz, $^3J_{HH}$ = 7.2 Hz). – ^{13}C NMR (90.6 MHz, 263 K, [D$_5$]pyridine): δ = 157.5 (*p*-C, Ph), 157.4 (*p*-C′, Ph), 147.2 (d, *i*-C, Ph, $^3J_{PC}$ = 1.4 Hz), 143.2 (d, *i*-C′, Ph, $^3J_{PC}$ = 13.9 Hz), 136.4 (d, *o*-C, Ph_2P, $^2J_{PC}$ = 8.3 Hz), 134.0 (d, *o*-C′, Ph_2P, $^2J_{PC}$ = 6.9 Hz), 132.2 (d, *p*-C, Ph_2P, $^4J_{PC}$ = 2.1 Hz), 131.8 (d, *p*-C′, Ph_2P, $^4J_{PC}$ = 2.1 Hz), 130.1 (*o*-C, Ph), 129.4

(d, *m*-C, Ph_2P, $^3J_{PC}$ = 9.7 Hz), 129.0 (*o*-C′, Ph), 128.3 (d, *m*-C′, Ph_2P, $^3J_{PC}$ = 12.5 Hz), 126.3 (d, *i*-C, Ph_2P, $^1J_{PC}$ = 92.3 Hz), ca. 123 (*i*-C′, Ph_2P, obscured), 113.0 (*m*-C, Ph), 112.5 (*m*-C′, Ph), 58.3 (s, C-4, $^2J_{PC}$ = 0 Hz), 57.4 (d, C-3, $^1J_{PC}$ = 70.1 Hz), 54.9 (OCH_3), 54.8 (OCH_3'), 23.7 (d, P*C*H_2CH_3, $^1J_{PC}$ = 56.2 Hz), 16.1 (d, PCH*C*H_3, $^2J_{PC}$ = 3.5 Hz), 8.8 (d, PCH_2*C*H_3, $^2J_{PC}$ = 6.2 Hz). − ^{31}P NMR (81.0 MHz, 253 K, [D$_5$]pyridine): δ = 16.8; (263 K): δ = 14.4; (273 K): δ = 12.4. − 17 mg (70 µmol) of (ethyl)(ethylidene)diphenylphosphorane was treated with 17 mg (66 µmol) of 4,4′-dimethoxythiobenzophenone in ca. 0.6 mL of [D$_2$]dichloromethane at −78°C. − ^{1}H NMR (360.1 MHz, 243 K, [D$_2$]dichloromethane): δ = 8.10 (d, 2 H, *o*-H, Ph, $^3J_{HH}$ = 8.8 Hz), 7.87 (d, 2 H, *o*-H′, Ph, $^3J_{HH}$ = 8.8 Hz), 7.68−7.53 (m, 6 H, *o*-H, *o*-H′, *p*-H, *p*-H′, PPh_2), 7.46 (m, 4 H, *m*-H, *m*-H′, PPh_2), 6.72 (d, 2 H, *m*-H, Ph, $^3J_{HH}$ = 8.8 Hz), 6.60 (d, 2 H, *m*-H′, Ph, $^3J_{HH}$ = 8.8 Hz), 4.78 (dq, 1 H, PC*H*CH_3, $^2J_{PH}$ = 3.3 Hz, $^3J_{HH}$ = 6.6 Hz), 4.06 (m, 1 H, PCHH′), 3.74, 3.65 (s, each 3 H, OCH_3, OCH_3'), 2.30 (m, 1 H, PCHH′), 1.30 (dd, 3 H, PCHC*H*$_3$, $^2J_{PH}$ = 20.4 Hz, $^3J_{HH}$ = 6.6 Hz), 0.67 (dt, 3 H, PCH_2C*H*$_3$, $^2J_{PH}$ = 20.4 Hz, $^3J_{HH}$ = 7.7 Hz). − ^{13}C NMR (90.6 MHz, 243 K, [D$_2$]dichloromethane): δ = 156.6 (*p*-C, Ph), 156.4 (*p*-C′, Ph), 145.7 (d, *i*-C, Ph, $^3J_{PC}$ = 1.6 Hz), 141.8 (d, *i*-C′, Ph, $^3J_{PC}$ = 13.7 Hz), 135.9 (d, *o*-C, Ph_2P, $^2J_{PC}$ = 8.4 Hz), 133.0 (d, *o*-C′, Ph_2P, $^2J_{PC}$ = 6.8 Hz), 132.6 (d, *p*-C, Ph_2P, $^4J_{PC}$ = 3.2 Hz), 132.1 (d, *p*-C′, Ph_2P, $^4J_{PC}$ = 2.6 Hz), 129.8 (*o*-C, Ph), 129.2 (d, *m*-C, Ph_2P, $^3J_{PC}$ = 10.5 Hz), 129.17 (*o*-C′, Ph), 128.1 (d, *m*-C′, Ph_2P, $^3J_{PC}$ = 12.1 Hz), 124.4 (d, *i*-C, Ph_2P, $^1J_{PC}$ = 68.4 Hz), 121.5 (d, *i*-C′, Ph_2P, $^1J_{PC}$ = 88.4 Hz), 112.2 (*m*-C, Ph), 111.6 (*m*-C′, Ph), 57.9 (s, C-4, $^2J_{PC}$ = 0 Hz), 55.0 (OCH_3), 54.9 (OCH_3'), 52.6 (d, C-3, $^1J_{PC}$ = 62.6 Hz), 20.9 (d, P*C*H_2CH_3, $^1J_{PC}$ = 52.1 Hz), 15.8 (d, PCH*C*H_3, $^2J_{PC}$ = 3.2 Hz), 8.3 (d, PCH_2*C*H_3, $^2J_{PC}$ = 6.3 Hz). − ^{31}P NMR (81.0 MHz, 233 K, [D$_2$]dichloromethane): δ = 27.9; (243 K): δ = 26.5; (253 K): δ = 25.3.

(±)-Thiabetaine 5i: 11 mg (57 µmol) of diethyl(ethylidene)(phenyl)-phosphorane was treated with 16 mg (62 µmol) of 4,4′-dimethoxythiobenzophenone in ca. 0.6 mL of [D$_5$]pyridine at −35°C. − ^{1}H NMR (360.1 MHz, 268 K, [D$_5$]pyridine): δ = 8.76 (d, 2 H, *o*-H, Ph, $^3J_{HH}$ = 8.8 Hz), 8.38 (d, 2 H, *o*-H′, Ph, $^3J_{HH}$ = 8.8 Hz), 8.13 (m, 2 H, *o*-H, PhP), 7.47 (m, 3 H, *m*-, *p*-H, PhP), 7.03 (d, 2 H, *m*-H, Ph, $^3J_{HH}$ = 8.8 Hz), 6.86 (d, 2 H, *m*-H′, Ph, $^3J_{HH}$ = 8.8 Hz), 4.83 (q, 1 H, PC*H*CH_3, $^2J_{PH}$ = 0 Hz, $^3J_{HH}$ = 6.7 Hz), 3.59 (s, 3 H, OCH_3), 3.55 (m, 1 H, C*H*H′ or CH*H*′), 3.49 (s, 3 H, OCH_3'), 3.08, 2.66, 2.12 (m, each 1 H, C*H*H′ or CH*H*′), 1.56 (dd, 3 H, PCHC*H*$_3$, $^3J_{PH}$ = 20.4 Hz, $^3J_{HH}$ = 6.7 Hz), 0.96 (m, 6 H, PCH_2C*H*$_3$, $^3J_{PH}$,$^3J_{HH}$ not determined). − ^{13}C NMR (90.6 MHz, 268 K, [D$_5$]pyridine): δ = 157.3 (*p*-C, Ph), 157.2 (*p*-C′, Ph), 147.5 (s, *i*-C, Ph, $^3J_{PC}$ = 0 Hz), 143.6 (d, *i*-C′, Ph, $^3J_{PC}$ = 13.7 Hz), 134.3 (d, *o*-C, PhP, $^2J_{PC}$ = 6.3 Hz), 132.0 (d, *p*-C, PhP, $^4J_{PC}$ = 2.1 Hz), 130.2 (*o*-C, Ph), 128.8 (*o*-C′, Ph), 128.81 (d, *m*-C, PhP, $^3J_{PC}$ = 10.5 Hz), 125.6 (d, *i*-C, PhP, $^1J_{PC}$ = 76.8 Hz), 112.9 (*m*-C, Ph), 112.5 (*m*-C′, Ph), 58.2 (d, C-4, $^2J_{PC}$ = 0 Hz), 55.0, 54.9 (OCH_3 and OCH_3'), 53.8 (d, C-3, $^1J_{PC}$ = 67.4 Hz), 17.8 (d, PCH_2, $^1J_{PC}$ = 55.8 Hz), 16.7 (d, PCH_2, $^1J_{PC}$ = 45.3 Hz), 14.7 (d, PCH*C*H_3, $^2J_{PC}$ = 5.3 Hz), 7.76, 7.68 (d, PCH_2*C*H_3, $^2J_{PC}$ = 5.3 Hz). − ^{31}P NMR (242.9 MHz, 243 K, [D$_5$]pyridine): δ = +27.6; (263 K): δ = +25.6; (268 K): δ = +25.3.

(±)-Thiabetaine 10: 87 mg (0.34 mmol) of 4,4′-dimethoxythiobenzophenone in 2 mL of THF was added to 50 mg (0.34 mmol) of triethyl(ethylidene)phosphorane in 5 mL of pentane at 0°C. The supernatant solution was removed and the precipitate washed 5 times with 5 mL of pentane. The collected solid was dried in vacuo. − ^{1}H NMR (599.9 MHz, 298 K, [D$_5$]pyridine): δ = 8.62 (d, 2 H, *o*-H, Ph, $^3J_{HH}$ = 9.0 Hz), 8.39 (d, 2 H, *o*-H′, Ph, $^3J_{HH}$ = 9.0 Hz), 6.97 (d, 2 H, *m*-H, Ph, $^3J_{HH}$ = 9.0 Hz), 6.89 (d, 2 H, *m*-H′, Ph, $^3J_{HH}$ = 9.0 Hz), 4.65 (dq, 1 H, PC*H*CH_3, $^2J_{PH}$ = 2.4 Hz, $^3J_{HH}$ = 6.8 Hz), 3.62, 3.58 (s, each 3 H, OCH_3, OCH_3'), 2.60, 2.17 (m, each 3 H, C*H*H′, CH*H*′), 1.57 (dd, 3 H, PCHC*H*$_3$, $^3J_{PH}$ = 19.0 Hz, $^3J_{HH}$ = 6.8 Hz), 1.03 (dt, 9 H, PCH_2CH_3, $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 7.6 Hz). − ^{13}C NMR (150.8 MHz, 298 K, [D$_5$]pyridine): δ = 157.6 (*p*-C, Ph), 157.4 (*p*-C′, Ph), 147.7 (s, *i*-C, Ph, $^3J_{PC}$ = 0 Hz), 144.1 (d, *i*-C′, Ph, $^3J_{PC}$ = 12.9 Hz), 131.1 (*o*-C, Ph), 130.1 (*o*-C′, Ph), 112.8 (*m*-C, Ph), 112.5 (*m*-C′, Ph), 55.07 (OCH_3), 55.03 (OCH_3'), 57.6 (d, C-4, $^2J_{PC}$ = 0 Hz), 48.5 (d, C-3, $^1J_{PC}$ = 67.7 Hz), 16.8 (d, PCH_2, $^1J_{PC}$ = 51.8 Hz), 14.6 (d, PCH*C*H_3, $^2J_{PC}$ = 4.0 Hz), 7.7 (d, PCH_2*C*H_3, $^2J_{PC}$ = 5.5 Hz). − ^{31}P NMR (242.9 MHz, 243 K, [D$_5$]pyridine): δ = +31.0; (263 K): δ = +29.8; (283 K): δ = 28.5; (298 K): δ = +27.5.

Acknowledgments

Financial support from the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, and the Ministerium für Schule, Weiterbildung, Wissenschaft und Forschung des Landes Nordrhein-Westfalen is gratefully acknowledged.

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Received March 1, 1999
[O99121]