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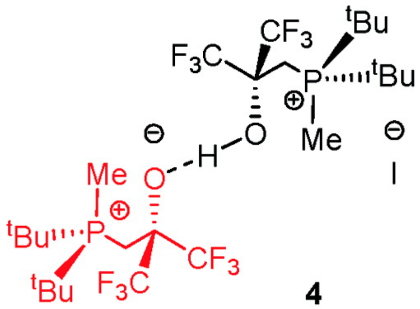

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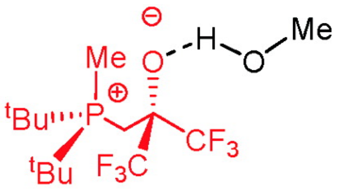

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A Stabilized *β*-Oxaphosphoniumbetaine: An Elusive Zwitterion

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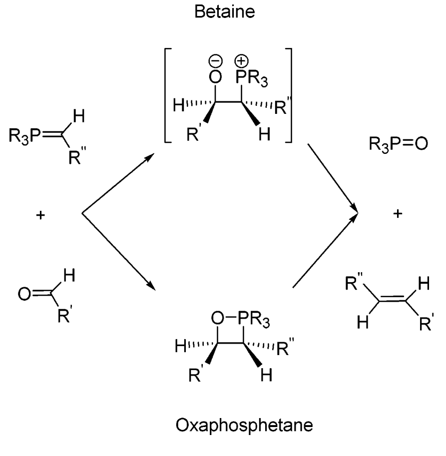
Abstract: A *β*-oxaphosphoniumbetaine stabilized by two *tert*-butyl groups at the phosphonium part of the betaine and two trifluoromethyl groups at the carbon adjoined to the oxa part of the betaine was isolated and structurally characterized. Additional stabilization results from the solvation of the betaine by a parent phosphonium salt, as in **4**, or by protonation with methanol, as in **10**. According to X-ray analysis, the betaine exhibits a sterically strained "gauche" conformeric form, with torsion angles in the P−C−C−O moiety of 32.2° for **4** and 28.1° for **10**. The P···O separations of 3.121 Å for **4** and 3.086 Å for **10** are just under the sum of the O and P van der Waals radii (3.32 Å). The fast H/D exchange of α hydrogen atoms to the phosphonium center was observed in the solution of **10** in deuterium oxide and MeOH-*d*$_4$. The *β*-oxaphosphoniumbetaine has long been suspected as an intermediate in the Wittig reaction, but this is the first time a stabilized derivative has been isolated.

Introduction

Indisputably, the widest applications of organophosphorus compounds are in the Wittig reactions and the related Wadsworth−Emmons condensations.[1] These reactions are of fundamental importance in organic chemistry, and innumerable syntheses of complex natural products and pharmaceutical compounds have been achieved using these organophosphorus compounds. Substantial effort has been applied to identifying the intermediates present in the Wittig reactions. However, it has not yet been conclusively demonstrated whether such reactions go through betaine or oxaphosphetane intermediates (Scheme 1). Early work pointed toward the betaine intermediate, but more recent experimental studies have favored the oxaphosphetane intermediate.[2]

A betaine lithium salt was observed during the course of the Wittig reaction, but it was not isolated and structurally characterized.[3] Outside of Wittig chemistry, *β*-oxaphosphoniumbetaine remains elusive to isolation, although thia analogs are known.[4] A phosphorus−sulfur bond is weaker than a phosphorus−oxygen bond thermodynamically, and this should make the formation of a thiaphosphetane less favorable than formation of an oxaphosphetane. Interest in phosphoniumbetaines has sharply increased recently because they are phosphorus analogs of organo amino acids, with a wide spectrum of potential chemical and biological properties.[5]

Scheme 1



Theoretical calculations[2,5a] suggest that solvation by a proton-donating reagent and increasing steric bulk around the phosphorus and carbon atoms should favor stabilization of the betaine and decrease the tendency for four-membered ring closure. Additionally, introduction of electron-withdrawing groups at the carbon atom should stabilize the negative charge at oxygen.

Recently, we have shown that a new chelating phosphine $^{t}Bu_2P-CH_2-C(CF_3)_2OH$ **1** with a sterically bulky "soft" di-*tert*-butyl phosphine center and a bulky "hard" fluorinated alkoxy center can stabilize unusual coordination numbers of

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(1) Quin, L. D. *A Guide to Organophosphorus Chemistry*; A John Wiley & Sons, Inc.: New York, 2000.

(2) (a) Seth, M.; Senn, H. M.; Ziegler, T. *J. Phys. Chem. A* **2005**, *109*, 5136 and references therein. (b) McEwen, W. E.; Mari, F.; Lahti, P. M.; Baughman, L. L.; Ward, W. J., Jr. In *Phosphorus Chemistry. Development in American Science*; Walsh, E. N., Griffith, E. J., Parry, R. W., Quin, L. D., Eds.; American Chemical Society: Washington, DC, 1992; Vol. 486, p 149.

(3) (a) Geletneky, C.; Forsterling, F.-H.; Bock, W.; Berger, S. *Chem. Ber.* **1993**, *126*, 2397. (b) Neumann, R.; Berger, S. *Eur. J. Org. Chem.* **1998**, 1085.

(4) Zemlyansky, N. N.; Borisova, I. V.; Ustynyuk, Y. A. *Adv. Organomet. Chem.* **2004**, *49*, 35 and references therein.

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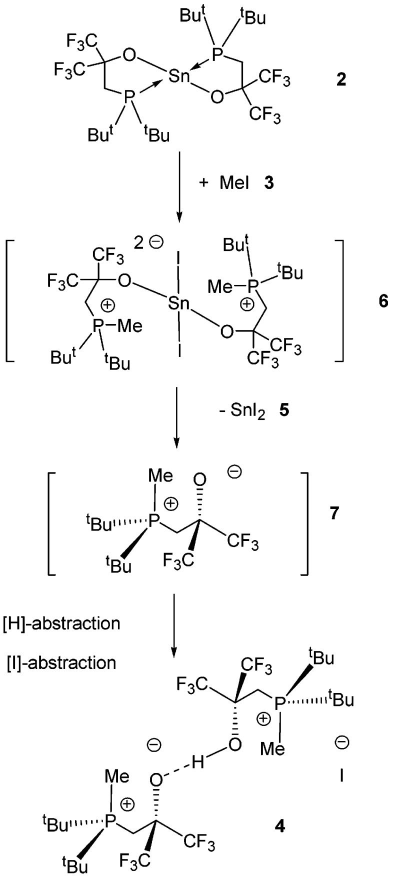
Scheme 2



iridium and can stabilize the divalent germanium and tin compounds.[6]

The pattern of substitution of this β-oxyphosphine fits theoretical models for the stabilization of β-oxaphosphonium-betaine. To test this, we carried out the alkylation reaction of the divalent tin compounds stabilized by this P^O chelating phosphine. Oxidizing reagents, e.g., sulfur, pyridine-*N*-oxide, and 1-azidoadamantane, have been shown to react with the divalent tin at the phosphorus ligands exclusively, preserving the divalent state of tin.[6b] The reaction with methyl iodide would be expected to transform phosphorus atoms to methylphosphonium groups, which would be unable to coordinate with the central tin atom. This would be expected to destabilize the complex and lead to fragmentation of the intermediate complex, yielding the β-oxaphosphoniumbetaine. The results will be discussed in the following sections.

Results and Discussion

Reaction between *trans*-bis[3-(di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoromethyl)-2-propano-lato-O,P]tin(II) **2** and iodomethane **3** took 1 month to complete at room temperature in THF. Two products were isolated from this reaction: a di-*tert*-butyl-methyl-(3,3,3-trifluoro-2-oxa-2-trifluoro-methyl-propyl)-phosphoniumbetaine adduct with di-*tert*-butyl-methyl-(3,3,3-trifluoro-2-hydroxy-2-trifluoromethyl-propyl)-phosphonium iodide **4** and tin(II) iodide **5** (Scheme 2).

The betaine adduct with parent phosphonium salt **4** is a high-melting crystalline solid that is almost insoluble in nonpolar organic solvents and mostly exhibits poor solubility in polar organic solvents.

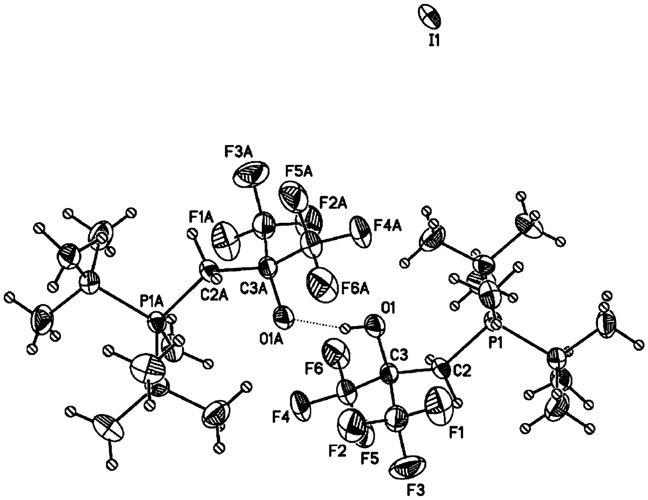


Figure 1. ORTEP drawing of di-*tert*-butyl-methyl-(3,3,3-trifluoro-2-oxa-2-trifluoromethyl-propyl)-phosphonium betaine adduct with di-*tert*-butyl-methyl-(3,3,3-trifluoro-2-hydroxy-2-trifluoromethyl-propyl)-phosphonium iodide **4**. A crystal was grown from a 1:1:1 mixture of THF/toluene/pentane. Thermal ellipsoids are drawn to the 50% probability level.

According to X-ray analysis of **4**, there is one iodine per two phosphorus atoms in the crystal structure (Figure 1). The molecule is disordered with a center of symmetry between neighboring oxygen atoms, indicating an averaging of betaine and phosphonium moieties in the solid state. The betaine and phosphonium moieties in **4** are connected to each other by hydrogen bonding between the anionic oxygen atom of the betaine and the hydroxyl hydrogen of the phosphonium part.

Consistent with the structure in the solid state, the ^{31}P NMR spectrum of **4** has one broad line at 51.68 ppm with a half-width of the line at 28 Hz for both phosphorus atoms (betaine and phosphonium). The broadening of lines, which is typical for the betaines in general, was also observed in ^{1}H and ^{19}F NMR spectra of **4** (see the Experimental Section).

Tin(II) iodide **5** was the only tin-containing product isolated from the above reaction by slow sublimation of the residue left from the recrystallization experiments of the reaction mixture. The structure of SnI$_2$ was proven by X-ray analysis. The unit cell parameters for the red-orange sublimate matched the unit cell parameters for SnI$_2$ previously done at 23 °C.[7]

A plausible mechanism for the formation of **4** includes initial methylation of the phosphorus atoms in **2** by methyl iodide. The resulting intermediate complex **6** would have two nonchelating ligands and two iodides coordinated to the central tin atom. Fragmentation of complex **6** would give SnI$_2$ **5** and two molecules of nonsolvated β-oxaphosphoniumbetaine **7**. Further stabilization of the two betaines **7** by hydrogen and iodine abstractions from the excess iodomethane would lead to the stable adduct of betaine with a parent phosphonium salt **4**. Iodomethane is known to serve as a source of HI or hydrogen and iodine separately.[8]

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(6) (a) Ionkin, A. S.; Marshall, W. J. *Organometallics* **2004**, *23*, 6031. (b) Ionkin, A. S.; Marshall, W. J.; Fish, B. M. *Organometallics* **2006**, *25*, 4170.

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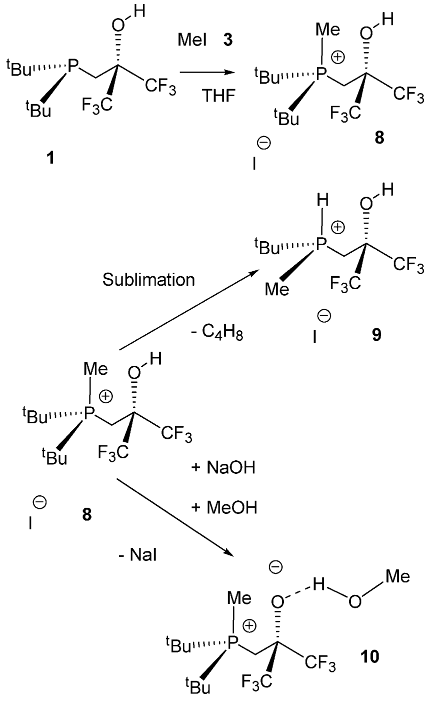
Scheme 3



Having demonstrated that the pattern of the substitution of this β-hydroxyphosphine stabilizes β-oxaphosphoniumbetaine, we decided to search for a more straightforward method of generating betaine **7**. Deprotonation of β-hydroxyphosphonium salt **8** in the presence of alkoxide ion in protic solvents was selected as an alternative method for generating betaine **7**. Historically, it was one of the first methods to generate β-oxaphosphoniumbetaines *in situ*.[9,10] Salt **8** was synthesized by the quaternization of β-hydroxyphosphine **1**[6a] with iodomethane **3** (Scheme 3).

The first attempt to deprotonate β-hydroxyphosphonium salt **8** by elimination of HI by sublimation *in vacuo* resulted in the elimination of isobutene from one of the *tert*-butyl groups of **8**, yielding P−H phosphonium salt **9**. Similar elimination of isobutene from sterically overcrowded phosphines has been noted.[11] Deprotonation of **8** at room temperature with sodium hydroxide in methanol was more successful and resulted in the isolation of betaine **10** stabilized by one molecule of the solvent.

The ^{31}P NMR resonance of betaine **10** was observed at 49.31 ppm in MeOH-d_4. Signals for phosphonium salt **8** (50.81 ppm) and another betaine adduct **4** (51.68 ppm) were also observed. Chemical shifts for the phosphonium salt and betaine adducts are essentially the same in MeOH-d_4 and MeCN-d_3.

The major difference between the betaine and the parent phosphonium salt was observed in a hydrogen/deuterium (H/D) exchange process. The parent salt **8** dissolved in D_2O or MeOH-d_4 does not undergo H/D exchange of methylene protons in the α position to the phosphorus. In contrast, betaine **10** dissolved in D_2O or MeOH-d_4 shows H/D exchange instantly. Two additional signals with monodeuterated (**10b**) and dideuterated (**10c**) species also appeared in the ^{31}P NMR spectrum of **10** (Figure 2C). Heating a solution of **10** in deuterium oxide at 90 °C for 1 h completely transformed betaine **10** into dideuterated species **10c** (Figure 2A). A sample of **10** run in H_2O using a D_2O capillary as a lock showed only one singlet at 48.78 ppm (Figure 2B). During the same process complete loss of methylene protons was recorded in the ^{1}H NMR spectra due to H/D exchange. The ^{2}D NMR spectra of **10c** reveal a signal at 2.54 ppm, corresponding to P−CD_2 deuterons. The protonated methylene resonances in the ^{1}H NMR spectra of **10** and monodeuterated (**10b**) species were observed at 2.58 and 2.56 ppm, respectively.

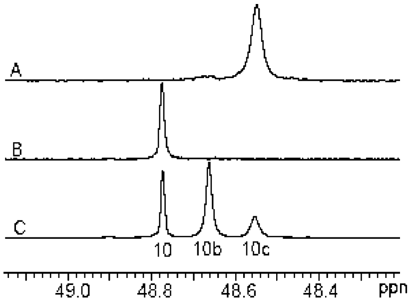
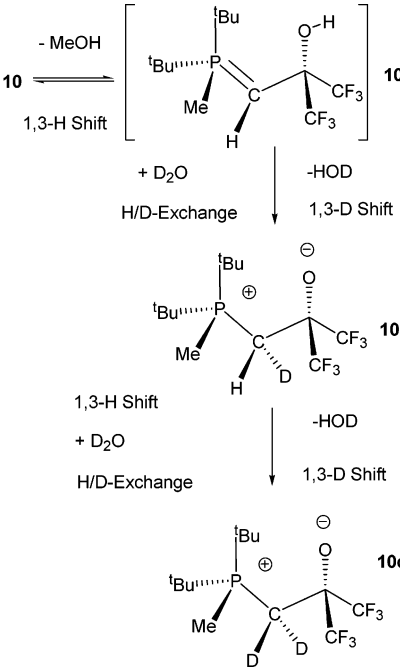


Figure 2. Hydrogen/deuterium (H/D) exchange process in D_2O observed in ^{31}P NMR spectra of **10**: (A) sample run in D_2O after heating for 1 h at 90 °C; (B) sample run in H_2O using a D_2O capillary as lock; (C) sample run in D_2O at 25 °C.

Scheme 4. Plausible H/D Exchange Mechanism of **10**[a]



[a] The hydrogen bonding of oxa-atom with methanol and water/deuterium oxide are omitted mostly for clarity.

This phenomenon is a common feature of phosphabetaines with hydrogen atoms α to the phosphonium center because they are capable of forming the tautomeric ylide intermediates, like **10a** in Scheme 4, facilitating the H/D exchange.[12]

Solid-State Structures of Phosphonium Salts and Betaines. The common structural feature of phosphonium salts and betaines is that they all exist as a sterically strained “gauche”

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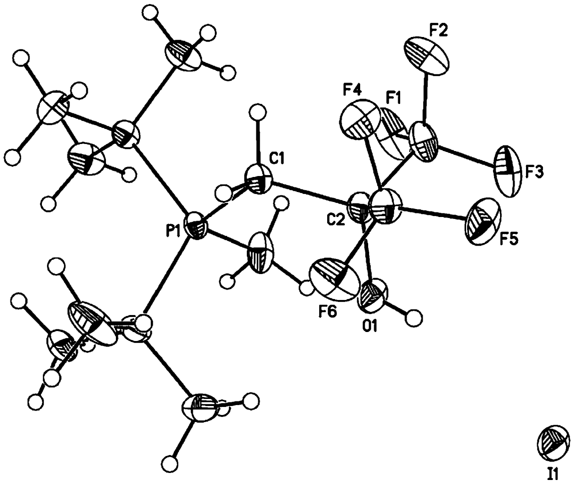

Figure 3. ORTEP drawing of di-*tert*-butyl-methyl-(3,3,3-trifluoro-2-hydroxy-2-trifluoromethyl-propyl)-phosphonium iodide **8**. A crystal was grown from a 3:1 mixture of THF and pentane. Thermal ellipsoids are drawn to the 50% probability level.

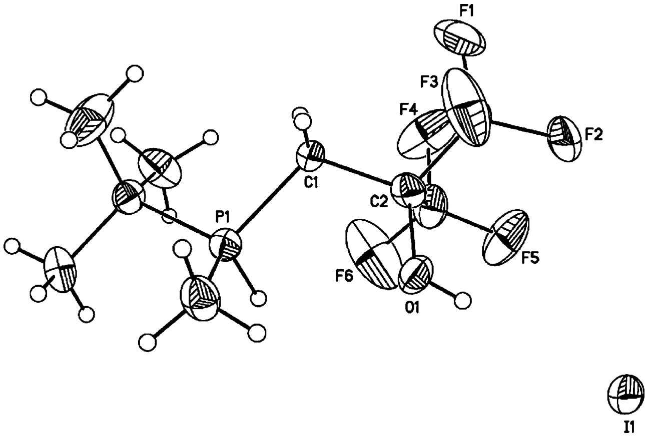

Figure 4. ORTEP drawing of *tert*-butyl-methyl-(3,3,3-trifluoro-2-hydroxy-2-trifluoromethyl-propyl)-phosphonium iodide **9**. A crystal was grown from acetonitrile. Thermal ellipsoids are drawn to the 50% probability level.

conformer (Figures 1, 3−5). It is strained because the torsion angles lie between "eclipsed" and "gauche" forms. This "gauche" conformer is probably stabilized by the electrostatic interaction between the charges on the P and O atoms (Coulombic attraction between the cationic and anionic centers[13]). The torsion angles do not change significantly moving from phosphonium to betaine moieties with the same steric environment, e.g., from structure **8** to **10** (angles: 28.3° and 28.1°). However, decreasing the steric hindrance around the phosphorus by replacing one *tert*-butyl group by a hydrogen in phosphonium salts **8** and **9** resulted in a shift of torsion angles toward a classical "gauche" conformation (from 28.3° for **8** to 44.6° for one of the stereoisomers of **9**). There is a shortening of C−O and P−C bond lengths upon the formation of the betaine from the phosphonium salt (0.05 and 0.01 Å, respectively). The central C−C bond in the P−C−C−O linkage undergoes elongation by 0.04 Å upon betaine formation.

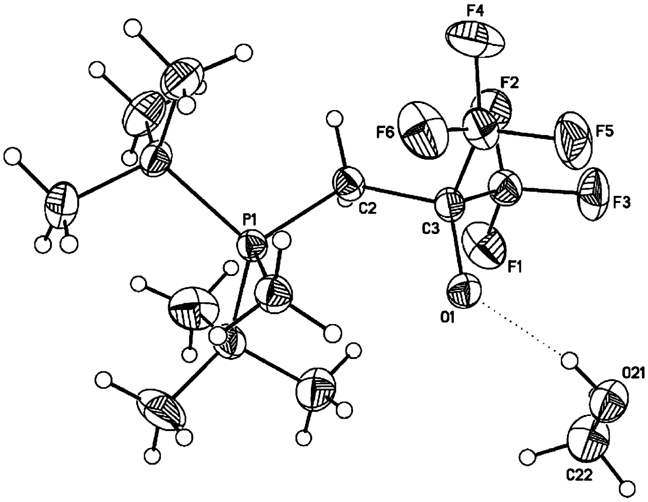

Figure 5. ORTEP drawing of di-*tert*-butyl-methyl-(3,3,3-trifluoro-2-oxa-2-trifluoromethyl-propyl)-phosphonium betaine **10** as an adduct with methanol. Attempts were made to find a hydrogen atom on O1, but none were seen in a difference map. There is also no reasonable place for a second OH hydrogen bonding with O1. Thermal ellipsoids are drawn to the 50% probability level.

The $P\cdots O$ separations for phosphonium salts and betaines (Table 1, second column) are very close to each other and just within the sum of O and P van der Waals radii (3.32[14] and 3.30 Å[15]). However, the $P\cdots O$ separations are substantially larger than a P−O single bond (e.g., 1.57 Å).[16]

Since the $P\cdots F$ separations for phosphonium salt **8** and all betaines are larger than the sum of P and F van der Waals radii (3.27 Å),[17] there should be no substantial stabilization through space between P and F. In the less sterically hindered phosphonium salt **9**, $P\cdots F$ separations are less than the sum of P and F van der Waals radii, creating the possibility that such through-space Coulombic interactions are plausible. In general, the structures of β-oxaphosphoniumbetaines synthesized in this study resemble the structures of P−C−C−S betaines.[4,18]

According to X-ray analysis, a molecule of methanol is connected to the oxa part of the betaine in **10** by means of hydrogen bonding only. It does not undergo ionization to form a methoxy anion and the corresponding oxyalkylphosphonium cation. Separation of anionic and cationic moieties is still in the β-position, so by definition, **10** is an example of a betaine. For example, a clear pattern of separation of cationic and anionic parts of the molecule is seen for the parent salt **8**. ^{31}P NMR analysis of **10** in the solution does not reveal any upfield signals. Such signals would be expected from the formation of methoxyphosphorane upon the migration of methoxy anion to form a pentacoordinated phosphorus species or from the formation of oxaphosphetane.[19]

We undertook thermolysis experiments with **10** to search for the modes of the Wittig reactions, even though the pattern of substitution in this β-oxaphosphoniumbetaine was designed to stabilize the betaine only. Sublimation of **10** under the same

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Table 1. Selected Bond Lengths (Angstroms) and Angles (Degrees) for Phosphonium (**8** and **9**) and Betaine (**4** and **10**) Structures

	P···O separation	P–C–C–O torsion angle	P–C distance	C–C	C–O	P···F separation closest P–F distance
8	3.029	−28.3(4)	1.836(3)	1.541(4)	1.396(4)	3.333
	3.057	−26.7(4)	1.834(3)	1.542(4)	1.388(4)	3.378
9	2.882	−37.4(7)	1.823(6)	1.538(7)	1.392(6)	3.096
	2.901	−38.0(7)	1.822(6)	1.520(7)	1.391(7)	3.094
	2.956	−44.4(8)	1.811(6)	1.521(8)	1.389(7)	3.126
	2.963	−44.6(7)	1.815(5)	1.534(7)	1.369(6)	3.132
10	3.121	28.1(2)	1.824(19)	1.583(2)	1.331(2)	3.414
4	3.086	32.2(3)	1.828(3)	1.560(4)	1.349(4)	3.351

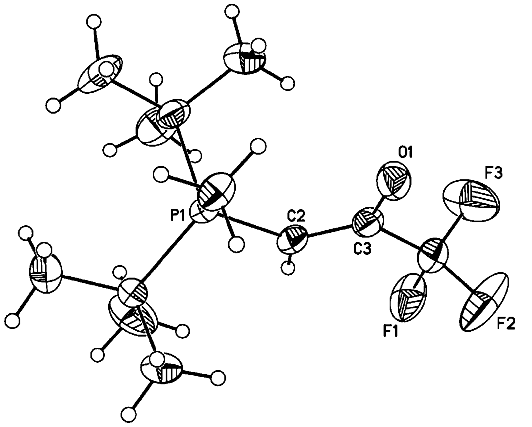
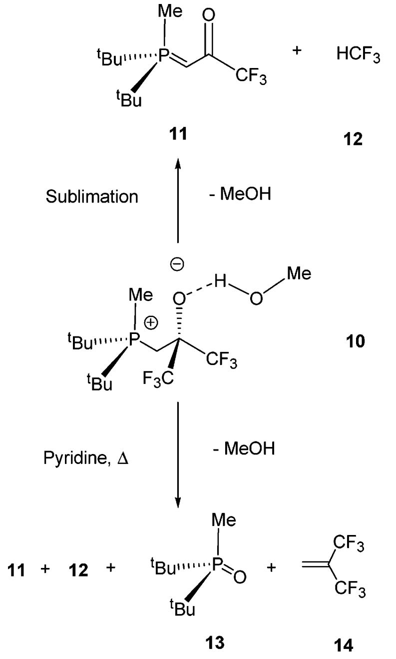


Figure 6. ORTEP drawing of 3-(di-*tert*-butyl-methyl-λ^5-phosphanylidene)-1,1,1-trifluoro-propan-2-one **11**. Thermal ellipsoids are drawn to the 50% probability level.

Scheme 5. Thermolysis of **10** in Different Conditions



conditions used for the sublimation of phosphonium salt **8** resulted in the formation of β-ketophosphorane **11** (Figure 6) by the elimination of trifluoromethane **12** from **10** (Scheme 5).

Heating a solution of **10** in deuterated pyridine afforded β-ketophosphorane **11** and di-*tert*-butyl-methylphosphine oxide **13** in a ratio of 78:22, according to ^{31}P NMR.[20] Di-*tert*-butyl-methylphosphine oxide **13** is an expected product of the Wittig reaction. Two possible unsaturated products can be anticipated here: 3,3,3-trifluoro-2-trifluoromethylpropene **14** from the decomposition of **10** by the Wittig route and 3,3,3-trifluoropropyne from the decomposition of **11** by the Wittig route. In the ^{19}F NMR spectrum, two major signals were observed: a singlet at −73.54 ppm for **11** and a characteristic doublet for trifluoromethane at −77.60 ppm (d, $^2J_{HF} = 79.3$ Hz).[21] A signal for 3,3,3-trifluoro-2-trifluoromethylpropene **14** was recorded at −65.12 ppm, but with low intensity (0.8%). This chemical shift was confirmed by the addition of a known sample of 3,3,3-trifluoro-2-trifluoromethylpropene **14** into the reaction mixture. Di-*tert*-butyl-methylphosphine oxide **13** and 3,3,3-trifluoro-2-trifluoromethylpropene **14** were also detected by GC/MS. No 3,3,3-trifluoropropyne was detected. Formation of acetylenes from β-ketophosphoranes is a known process, which usually takes place under pyrolytic conditions at 250−260 °C.[22,23]

In conclusion, two synthetic methods for the preparation of a stabilized β-oxaphosphoniumbetaine were developed. The stability likely results from steric protection by the two *tert*-butyl groups on the phosphonium part of the betaine and the electron-withdrawing ability of the two trifluoromethyl groups connected to the carbon of the oxa moiety of the betaine. Hydrogen bonding of the negative part of the betaine with the parent β-hydroxyphosphonium salt and with methanol also contributed to the stability of this β-oxaphosphoniumbetaine. We hope that our experimental evidence of β-oxaphosphoniumbetaine formation and its thermal degradation will be taken into account, when the Wittig reactions are being studied or used.

Experimental Section

All air-sensitive compounds were prepared and handled under a N_2/Ar atmosphere using standard Schlenk and inert-atmosphere box techniques. Anhydrous solvents were used in the reactions. Solvents were distilled from drying agents or passed through columns under an argon or nitrogen atmosphere. Iodomethane and THF were purchased from Aldrich.

Di-*tert*-butyl-methyl-(3,3,3-trifluoro-2-oxa-2-trifluoromethyl-propyl)-phosphoniumbetaine Adduct with Di-*tert*-butyl-methyl-(3,3,3-trifluoro-2-hydroxy-2-trifluoromethyl-propyl)-phosphonium Iodide (4) and Sn(II) Iodide (5). An amount of 1.24 g (0.00161 mol) of tin-(II), *trans*-bis[3-(di-*tert*-butylphosphino)-1,1,1-trifluoro-2-(trifluoro-methyl)-2-propanolato-O,P]- (**2**) and 0.69 g (0.00486 mol) of iodo-

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methane (**3**) were mixed in 50 mL of THF. The resultant crystals were filtered off after standing in the nitrogen glove box for 1 month. The solvent was removed in vacuo (1 mm of Hg), and the residue was sublimated in the tube sublimator. The red-orange sublimate was collected at 210 °C for 5 days at a pressure of 0.01 mm of Hg. The yield of di-*tert*-butyl-methyl-(3,3,3-trifluoro-2-oxa-2-trifluoromethyl-propyl)-phosphonium betaine adduct with di-*tert*-butyl-methyl-(3,3,3-trifluoro-2-hydroxy-2-trifluoromethyl-propyl)-phosphonium iodide (**4**) was 1.09 g (84%) as white crystals with mp 173−193 °C (decomposition). ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ 1.23 (d, $^3J_{PH} = 15.8$ Hz, 36H, Me), 1.19 (d, $^2J_{PH} = 12.5$ Hz, 6H, Me−P), 2.50 (br, 4H, CH_2−P), 9.50 (br, 1H, O−H). ^{19}F NMR (500 MHz, CD_3CN): δ −77.42 (br, 12F). ^{31}P NMR (500 MHz, CD_3CN): δ 51.68 (br, 2P). The structure was determined by X-ray analysis. The unit cell parameters for red-orange sublimate were determined at −100 °C to be monoclinic with $a = 14.179(3)$ Å, $b = 4.464(1)$ Å, $c = 10.836(3)$ Å, $\beta = 92.48(1)°$ in space group $C2/m$. This matched the unit cell parameters for SnI_2 (**5**) done previously at 23 °C with cell parameters $a = 14.17$ Å, $b = 4.535$ Å, $c = 10.87$ Å, $\beta = 92.0°$.[7] The yield of tin(II) iodide was 0.40 g (67%).

Di-*tert*-butyl-methyl-(3,3,3-trifluoro-2-hydroxy-2-trifluoromethyl-propyl)-phosphonium Iodide (8). An amount of 2.0 g (0.0061 mol) of 2-[(di-*tert*-butyl-phosphanyl)-methyl]-1,1,1,3,3,3-hexafluoro-propan-2-ol[6a] (**1**) was dissolved in 40 mL of THF. Then 0.96 g (0.0068 mol) of iodomethane (**3**) was added into the reaction mixture with stirring. After 3 days the solvent was removed in vacuo at 1 mm of Hg, and the residue was recrystallized from the 3:1 mixture of pentane and THF. The yield of di-*tert*-butyl-methyl-(3,3,3-trifluoro-2-hydroxy-2-trifluoromethyl-propyl)-phosphonium iodide (**8**) was 2.41 g (84%) as a white solid with mp 98.0 °C (sublimation). ^{1}H NMR (500 MHz, MeOH-d_4, TMS): δ 1.50 (d, $^3J_{PH} = 15.8$ Hz, 18H, Me), 2.11 (d, $^2J_{PH} = 12.8$ Hz, 3H, Me−P), 3.00 (d, $^2J_{PH} = 12.6$ Hz, 2H, CH_2−P), 7.0 (br, 1H, OH). ^{19}F NMR (500 MHz, MeOH-d_4): δ −78.61 (s, 6F). ^{31}P NMR (500 MHz, MeOH-d_4): δ 50.81. ^{1}H NMR (500 MHz, CD_3CN, TMS): δ 1.49 (d, $^3J_{PH} = 15.9$ Hz, 18H, Me), 2.09 (d, $^2J_{PH} = 12.7$ Hz, 3H, Me−P), 2.90 (d, $^2J_{PH} = 12.6$ Hz, 2H, CH_2−P). ^{19}F NMR (500 MHz, CD_3CN): δ −77.15 (s, 6F). ^{31}P NMR (500 MHz, CD_3CN): δ 51.96. The structure was determined by X-ray analysis.

***tert*-Butyl-methyl-(3,3,3-trifluoro-2-hydroxy-2-trifluoromethyl-propyl)-phosphonium Iodide (9).** An amount of 0.30 g (0.00064 mol) of di-*tert*-butyl-methyl-(3,3,3-trifluoro-2-hydroxy-2-trifluoromethyl-propyl)-phosphonium iodide (**8**) was charged in the glass boat and placed inside the tube sublimator. The sublimate was collected at 190 °C for 5 days and at a pressure of 0.01 mm of Hg. The resultant white sublimate was recrystallized from 0.5 mL of acetonitrile. The yield of *tert*-butyl-methyl-(3,3,3-trifluoro-2-hydroxy-2-trifluoromethyl-propyl)-phosphonium iodide (**9**) was 0.21 g (80%) as a white solid with mp 124.0−125.0 °C. ^{1}H NMR (500 MHz, CD_3CN, TMS): δ 1.20 (d, $^3J_{PH} = 18.5$ Hz, 9H, Me), 2.14 (d, $^2J_{PH} = 14.8$ Hz, 3H, Me−P), 3.05 (dd, $^2J_{PH} = 12.2$ Hz, $^3J_{HH} = 4.3$ Hz, 1H, CH_2−P), 3.37 (dd, $^2J_{PH} = 16.4$ Hz, $^3J_{HH} = 4.0$ Hz, 1H, CH_2−P), 7.00 (s, 1H, O−H), 7.10 (d, $^1J_{PH} = 507.3$ Hz, 1H, P−H). ^{19}F NMR (500 MHz, CD_3CN): δ −77.23 (m, 3F), −77.79 (m, 3F). ^{31}P NMR (500 MHz, CD_3CN): δ 17.54 (d, $^1J_{PH} = 507.3$ Hz). The structure was determined by X-ray analysis.

Di-*tert*-butyl-methyl-(3,3,3-trifluoro-2-oxa-2-trifluoromethyl-propyl)-phosphoniumbetaine Adduct with Methanol (10). An amount of 0.20 g (0.00043 mol) of di-*tert*-butyl-methyl-(3,3,3-trifluoro-2-hydroxy-2-trifluoromethyl-propyl)-phosphonium iodide (**8**) was dissolved in 15 mL of methanol, then 2.0 g of 50% water solution NaOH was added to the reaction mixture. The resultant crystals were filtered after 3 weeks. The yield of di-*tert*-butyl-methyl-(3,3,3-trifluoro-2-oxa-2-trifluoromethyl-propyl)-phosphonium betaine (**10**) was 0.09 g (62%) as a white solid with mp 185.0 °C (decomposition). ^{1}H NMR (500 MHz, run in H_2O using D_2O capillary as lock, TMS): δ 1.22 (d, $^3J_{PH} = 15.10$ Hz, 18H, Me), 1.85 (d, $^2J_{PH} = 13.44$ Hz, 3H, Me−P), 2.58 (d, $^2J_{PH} = 12.41$ Hz, 2H, CH_2−P), 3.20 (s, 3H, O−Me). ^{19}F NMR (500 MHz, run in H_2O using D_2O capillary as lock): δ −81.25 (br, 6F). ^{31}P NMR (400 MHz, VARIANS, run in H_2O using D_2O capillary as lock): δ 48.78 (s, 1P). The structure was determined by X-ray analysis.

3-(Di-*tert*-butyl-methyl-λ^5-phosphanylidene)-1,1,1-trifluoro-propan-2-one (11). An amount of 0.10 g (0.00027 mol) of di-*tert*-butyl-methyl-(3,3,3-trifluoro-2-oxa-2-trifluoromethyl-propyl)-phosphonium betaine (**10**) was charged in the glass boat and placed inside the tube sublimator. The sublimate was collected at 190 °C for 2 days and at a pressure of 0.01 mm of Hg. The yield of 3-(di-*tert*-butyl-methyl-λ^5-phosphanylidene)-1,1,1-trifluoro-propan-2-one (**11**) was 0.052 g (71%) as a white solid with mp 159−160 °C. ^{1}H NMR (500 MHz, CD_3CN, TMS): δ 1.38 (d, $^3J_{PH} = 14.7$ Hz, 18H, Me), 1.83 (d, $^2J_{PH} = 12.6$ Hz, 3H, Me−P), 3.60 (d, $^2J_{PH} = 14.3$ Hz, HC═P). ^{19}F NMR (500 MHz, CD_3CN): δ −73.95 (s, 3F). ^{31}P NMR (500 MHz, CD_3CN): δ 39.40 (s, 1P). The structure was determined by X-ray analysis.

Thermolysis of Di-*tert*-butyl-methyl-(3,3,3-trifluoro-2-oxa-2-trifluoromethyl-propyl)-phosphoniumbetaine Adduct with Methanol (10) in Pyridine. An amount of 0.20 g (0.00054 mol) of di-*tert*-butyl-methyl-(3,3,3-trifluoro-2-oxa-2-trifluoromethyl-propyl)-phosphonium betaine (**10**) and 0.20 mL of pyridine-d_5 were charged in a 5 mm NMR tube. The NMR tube was refluxed for 10 min and analyzed by NMR and mass spectrometry. According to ^{31}P NMR spectra the signal of starting compound **10** disappeared and two new signals were recorded: the signal at 60.43 ppm corresponding to di-*tert*-butyl-methylphosphine oxide (**13**) (lit. ^{31}P NMR (CCl_4): δ 60.00)[20] and signal of **11** at 39.37 ppm in a ratio of 22:78. According to ^{19}F NMR spectra, there is a singlet of **11** at - 73.54 ppm, a doublet of trifluoromethane at −77.60 ppm (d, $^2J_{FH} = 79.3$ Hz), and a singlet at −65.12 ppm for **14** (0.08%).[21] According to mass spectra, there are MH^+ ions at 271.14 ($C_{12}H_{22}FOP$) and 177.14 ($C_9H_{21}OP$) corresponding to **11** and **13**, and there is ion M^+ ion at 164.0 ($C_4H_2F_6$) for **14**.

X-ray Diffraction Studies. Data for all structures were collected using a Bruker CCD system at −100 °C. Structure solution and refinement were performed using the Shelxtl[24] set of programs. The A level alerts from Checkcif have all been addressed with the exception that hydrogen bond distances, and angles are not included for idealized riding hydrogens. For compound **9** errors exist that are due to problems with the convergence of the disordered solvent molecules.

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Supporting Information Available: Crystallographic information (CIF file) for complexes **4**, **8**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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