Propyne Iminium Salts and Phosphorus(III) Nucleophiles: Synthesis of (3-Morpholinoallenyl)phosphanes and -phosphane Oxides or 1-(Morpholinopropargyl)phosphanes and -phosphonates

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Treatment of 4-(1,3-diphenyl-l-propynylidene)morpholinium triflate (**1a**) with the neutral phosphorus nucleophiles $Me_3Si–PPh_2$, $Me_3Si–P(Ph)C_5H_{11}$, and $Me_3SiO–PPh_2$ affords (3-morpholinoallenyl)phosphanes **4** and **5** and (3-morpholinoallenyl)phosphane oxide **11**, respectively. In contrast to these conjugate addition reactions at the ambident propyne iminium moiety of **1a**, nucleophilic attack by $Me_3Si–PEt_2$ and $Me_3SiO–P(OEt)_2$ takes place at the iminium function and gives (1-morpholinopropargyl)phosphane **6** and (1-morpholinopropargyl)phosphonate **12**, respectively. Propyne iminium salt **1b** reacts with $Me_3Si–PPh_2$ to form (3-morpholino-1,3-butadienyl)phosphane oxide **8**. The bis(donor)-substituted allene **4** is transformed by oxidation of the phosphorus substituent into the push-pull substituted allenylphosphane oxide **11**. Treatment of allene **4** with elemental sulfur results in the formation of betaine **16**, which undergoes [3+2] cycloaddition reactions with acetylenic esters to afford 5-benzylidene-4,5-dihydrothiophenes **17** and **18**.

Introduction

Propyne iminium salts, featuring an iminium function in conjugation with a carbon−carbon triple bond, represent interesting building blocks for organic synthesis. Besides the cycloaddition potential of the activated C≡C bond,[1] addition of nucleophiles to the conjugated system determines the reactivity pattern. Because of the ambidentate nature of the propyne iminium unit, nucleophiles can either react at the iminium carbon atom (C-1 attack) to give propargylamines or enter into conjugate addition (C-3 attack), from which aminoallenes result. Thus, organolithium and -magnesium compounds engage both in C-1 and in C-3 attack,[2] while organocuprate addition reliably provides aminoallenes.[3] For S- and N-nucleophiles, we found that the regioselectivity was dependent on the nature of the nucleophile.[4] The results obtained with hetero-nucleophiles are by and large in agreement with the following interpretation: under kinetic control, both charge- and orbital-control favor C-1-attack but the reversibility of this reaction may finally provide the isomeric, thermodynamically more stable, aminoallenes.[4] We indeed found that a propargylic S,N-acetal formed under kinetic control underwent a proton-catalyzed rearrangement to a 3-(alkylthio)-1-morpholinoallene under thermodynamic control. However, other mechanistic details such as steric effects or metal coordination to the triple bond in the case of cuprates may override this simplistic explanation.

In continuation of these studies, we have investigated the reactions between propyne iminium salts and several phosphorus(III) nucleophiles, and we report here that the regioselectivity of the nucleophilic attack once more depends in a delicate manner on the nature of the nucleophilic reagent.

Results and Discussion

Silylated phosphanes react with α,β-unsaturated ketones or aldehydes to furnish, in general, products resulting from the conjugate addition of the nucleophilic phosphorus unit.[5] Analogously, (trimethylsilyl)phosphanes $Me_3Si–PR_2$ (PR_2 = PPh_2, PEt_2, 1-phospholanyl) undergo nucleophilic addition across the triple bond of acetylenic ketones.[6] It was therefore of interest to know whether silylphosphanes would behave analogously towards propyne iminium moieties. The reaction between propyne iminium triflate **1a** and diphenyl(trimethylsilyl)phosphane (**2a**) was investigated first, and after some experimentation, the following procedure was established (Scheme 1). A solution of the propyne iminium salt **1a** and anhydrous lithium chloride in THF was cooled to −78 °C and silylphosphane **2a** was added. The solution was brought to 20 °C over 12 h, the solvent was removed, and the residue was extracted first with pentane and then with toluene. From the toluene extract, 1-morpholino-3-(diphenylphosphanyl)allene **4** was obtained in good yield. This procedure was also used for the other nucleophilic addition reactions shown in Schemes 1 and 2.

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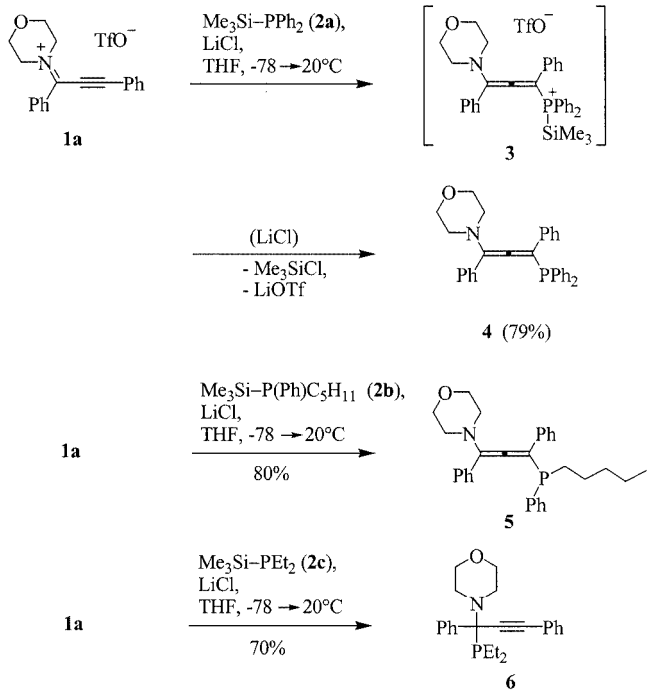
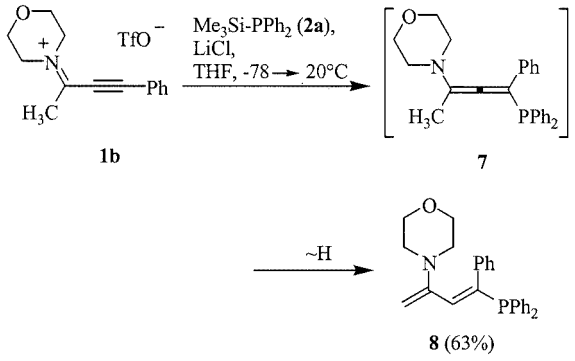


Scheme 1. Reaction between propyne iminium salt **1a** and phosphanes Me_3Si-PR_2

It is reasonable to assume that conjugated nucleophilic addition of silylphosphane **2a** initially produces the phosphonio-substituted aminoallene **3** (Scheme 1), which is converted into neutral allene **4** by chloride-induced desilylation, generating volatile chloro(trimethyl)silane and lithium triflate. In fact, when the reaction was carried out in the absence of LiCl, a ^{31}P NMR signal at $\delta = 11.2$ ppm was observed; it can be attributed to phosphonium salt **3** [compare: $\delta = 11.6$ ppm for the ion $MePh_2P^+$[(*Z*)-CH=CHPh)[7]] and disappears upon addition of LiCl. In the absence of LiCl, **3** slowly transformed over several days into allene **4**. However, salt **3** could not be isolated: removal of the solvent furnished a black oil, from which no defined compound could be isolated by extraction or distillation. It is likely that the highly electrophilic trimethylsilyl triflate, formed under these conditions, reacts with the enamine function of allene **4** and eventually initiates oligomerization.

Propyne iminium salt **1a** was also treated with two other silylphosphanes (Scheme 2). In analogy with the diphenyl-substituted phosphane **2a**, treatment with pentyl-phenyl-(trimethylsilyl)phosphane (**2b**) gave (3-morpholinoallenyl)-phosphane **5** (ca. 2:1 mixture of diastereomers) in good yield, but treatment with diethyl(trimethylsilyl)phosphane (**2c**) cleanly produced the (1-morpholinopropargyl)phosphane **6**. Thus, the replacement of two phenyl groups in the phosphorus nucleophile by two ethyl moieties causes a regioselectivity switch from C-3 to C-1 attack.

Silylphosphane **2a** also underwent conjugate addition with the 1-methyl-substituted propyne iminium salt **1b** (Scheme 2). In this case, however, the expected aminoallene



Scheme 2. Formation of a 2-dienamine from propyne iminium salt **1b**

7 could not be isolated, due to its rapid rearrangement into 1-(diphenylphosphanyl)-3-morpholino-1,3-butadiene **8**. The tautomeric 1,3-H shift is typical of aminoallenes bearing a CH substituent at either terminus of the allene unit and often prevents the isolation of these particular aminoallenes.[2]

It was fortunate that products **4**, **5**, and **8** could be isolated from the reaction mixture in almost pure form simply by toluene extraction, since the high hydrolytic lability of their enamine functionalities prevented chromatographic separation (see below).

If charge control were the dominant factor in the reaction between salt **1a** and anionic phosphorus nucleophiles, the addition of the diphenylphosphide anion could be expected to occur at the iminium carbon atom, resulting in the formation of P,N-acetal **9**. However, this product was not isolated when salt **1** was added to a THF solution of $KPPh_2$, generated in situ from chlorodiphenylphosphane and potassium, and allowed to react between −78 and 20 °C. NMR spectra and TLC indicated a rather complex product mixture, from which only one product could be isolated in pure form after chromatographic separation. This product was identified by a single-crystal X-ray structure analysis (Figure 1) as the 4-(morpholino)hex-2-en-5-yn-1-one **10**

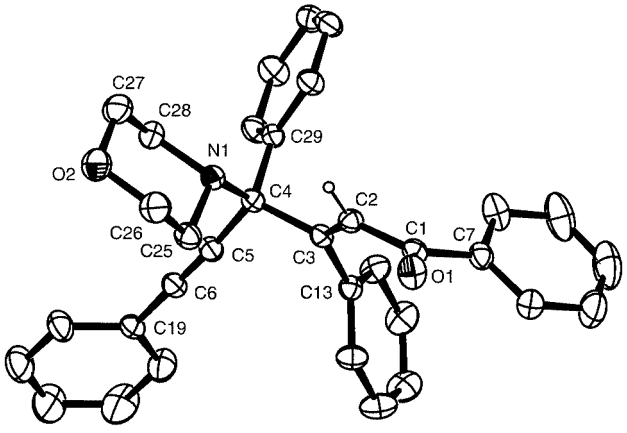
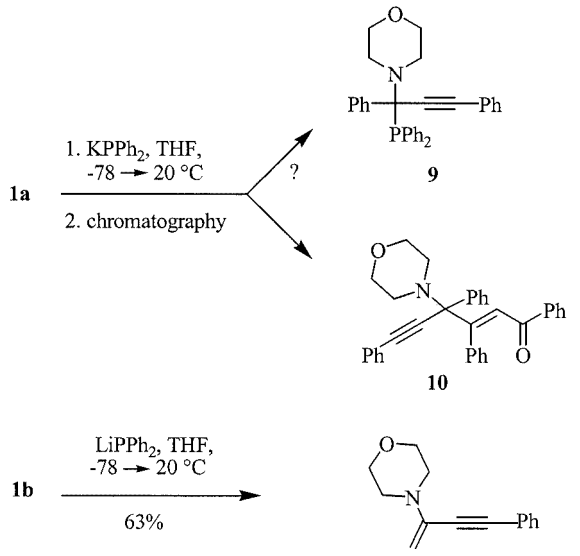
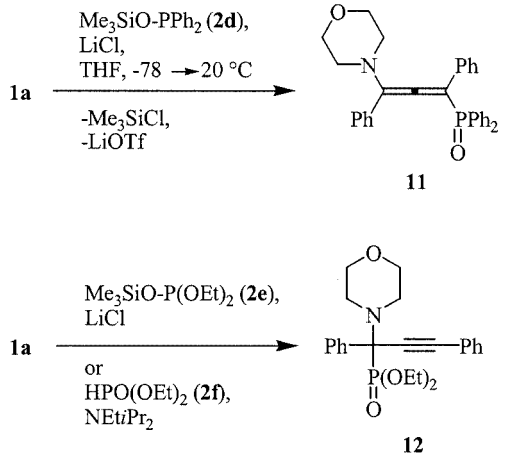


Figure 1. Structure of **10** in the crystal (ORTEP plot); ellipsoids of thermal vibration are shown at the 20% probability level; hydrogen atoms are omitted except for the olefinic H2; selected bond lengths [Å] and torsion angles [°]: C1−O1 1.222(2), C1−C2 1.483(3), C2−C3 1.332(2), C4−C5 1.486(3), C5−C6 1.192(2); O1−C1−C2−C3 −130.4(2)



Scheme 3. Reaction between propyne iminium salts **1a** and **1b** and potassium (or lithium) diphenylphosphide



Scheme 4. Reaction between propyne iminium salt **1a** and an *O*-silyl phosphonite or phosphite

(Scheme 3). It is obvious that **10** results from two cationic units of salt **1**, and it is likely that the 3-oxo-propenyl part of the molecule originates from a (morpholino)allene unit undergoing hydrolysis during chromatographic workup. Provided that this assumption is correct, the formation of **10** would include bond formation between the C-1 position of one propyne iminium cation and the C-3 position of another, and so between two acceptor positions. It may be speculated that the diphenylphosphide anion is involved in an umpolung step but the detailed mechanism is not yet known. When $KPPh_2$ was replaced by $NaPPh_2$ or $LiPPh_2$, compound **10** was also formed but it appeared that the reaction was even less clean than in the first case.

As expected, the diphenylphosphide anion behaved towards propyne iminium salt **1b** as a base rather than as a nucleophile. Treatment of **1b** with $LiPPh_2$ therefore gave *N*-[1-(phenylethynyl)vinyl]morpholine in 63% yield. We have reported previously that this deprotonation reaction can be performed conveniently with $KOSiMe_3$ as a base.[8]

Silylated phosphinites and phosphites are also known to undergo conjugate addition to α,β-unsaturated carbonyl compounds,[9] although 1,2-additions can occur as well (e.g., with acrolein[9b]). We found that they also add readily to propyne iminium salt **1a**. Thus, *O*-trimethylsilyl phosphinite **2d** reacted with **1a** in the presence of lithium chloride to form (3-morpholinoallenyl)phosphane oxide **11** in good yield (Scheme 4). Unlike the allenylphosphanes **4** and **5**, the more polar allene **11** is no longer soluble in toluene and therefore could not be isolated by extraction. More polar solvents (e.g. CH_2Cl_2) dissolve not only **11** but also some of the lithium triflate formed as a by-product, and again, the hydrolytic lability of **11** prevented its purification by chromatography. The same allene could be prepared independently by oxidation of allenylphosphane **4** (see below).

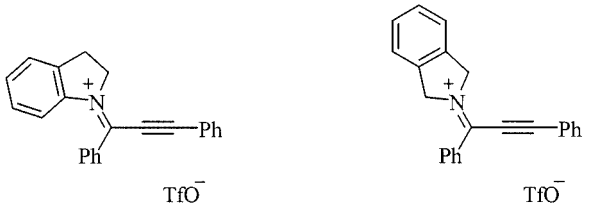
In mechanistic terms, the formation of **11** is related to that of **4**, shown in Scheme 1. Conjugate nucleophilic addition of **2d** generates a trimethylsilyloxy-phosphonium salt, which undergoes a Michaelis−Arbuzov type chloride-induced desilylation (with elimination of Me_3SiCl) accompanied by $P^{III} \rightarrow P^{V}$ conversion.

Trimethylsilyl phosphite **2e** also underwent a Michaelis−Arbuzov-type reaction with **1a**, but in this case the nucleophilic attack occurred at the iminium carbon atom and the (1-morpholinopropargyl)phosphonic acid ester **12** was obtained in 75% yield (Scheme 4). The same transformation was achieved in almost equal yield (69%) when diethyl phosphite (**2f**), rather than its derivative **2e**, was applied in the presence of a tertiary amine. The reaction between **1a** and **2e** is closely related to the recently reported formation of 1-amino-2-alkenyl phosphonates from the propene iminium salt $PhCH{=}CHCH{=}N^{+}Me_2$ Cl^{-} and trialkyl phosphites.[10]

In the hard and soft acids and bases model, neutral R_3P compounds rank as soft bases; the nucleophilicity decreases in the sequence R = alkyl > aryl > alkoxy while the hardness of the phosphorus atom increases in the same order.[11] If propyne iminium salts behaved as typical Michael acceptors, it would be expected that they would react with these nucleophiles preferentially by conjugate addition but that reaction at the iminium carbon atom would become more likely in the case of oxy-substituted phosphanes. The likeliness of conjugate addition should therefore decrease in the order **2c** > **2b** > **2a** > **2d** >**2e**. We found, however, that **2c** reacts at C-1 of the propyne iminium unit rather than at C-3. On the other hand, all these phosphorus nucleophiles would be expected to react under kinetic control at C-1, according to the same regioselectivity for charge- and orbital-controlled reactions[4] (see Introduction). Comparison of the bulkiness of these R_3P nucleophiles may explain the apparently conflicting results: although quantitative data for our silylated phosphane derivatives, such as the Tolman angle[12] and the pyramidality at phosphorus,[13] are not available, it can be stated qualitatively that the bulkiness decreases in the order **2a** > **2b** > **2d** > **2e** > **2c**. In fact, the first three compounds in the series undergo conjugate addition, while the last two add to the iminium carbon atom. It may therefore be argued that, under kinetic con-

trol, the phosphorus nucleophile preferentially approaches the iminium function (as predicted by the calculated values of atomic charge and LUMO coefficients[4]). However, since bond formation at C-1 generates two adjacent, densely substituted, quaternary centers, it is either a reversible reaction or completely inhibited energetically when the nucleophile becomes too bulky; in this case, C-3 attack, thanks to its less congested transition structure, can become more favorable energetically. In a quite different area, it has been found that the kinetics of ligand substitution of transition-metal carbonyls by phosphane derivatives depend both on electronic factors and on the bulkiness of the latter species.[14]

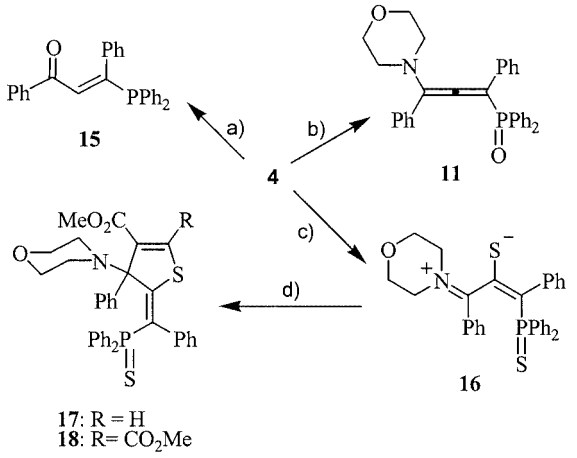
Since seemingly small changes in the R_2P-Z compound can alter the regioselectivity of the nucleophilic addition, it is not surprising that the exact nature of the propyne iminium moiety can have a similar effect. It is to be expected that a lower degree of charge stabilization in the iminium function should favor the formation and isolation of the product of nucleophilic addition at this position, since the reversibility of the addition is less likely. We indeed found that $Me_3SiOPPh_2$/LiCl reacts with propyne iminium salt **13** (Scheme 5) to give an inseparable mixture of the propargyl- and the allenylphosphane oxide, in which the former compound dominated by far. In contrast, the isomeric iminium salt **14** gave only the conjugate addition product (i.e., the allenylphosphane oxide), in complete analogy with **1a** and several other related salts possessing a well-stabilized *N*,*N*-dialkyliminium function.[15]



Scheme 5. Isomeric propyne iminium salts displaying different regioselectivity for nucleophilic addition of $Me_3Si-OPPh_2$

The chemistry of the novel electron-rich (3-morpholinoallenyl)phosphanes **4** and **5** would be expected to be dominated by transformations of the two reactive functionalities: the enamine moiety[16] and the (allenyl)phosphane unit.[17] This was confirmed by some transformations carried out with allene **4** (Scheme 6). The high hydrolytic lability of **4** has already been mentioned; in fact, it was readily hydrolyzed in contact with water to form the 3-(diphenylphosphanyl)prop-2-en-1-one **15**. Only one diastereomer was isolated, to which the *E* configuration was assigned from the small values of the phosphorus coupling of the olefinic proton ($^3J_{H,P}$ = 3.5 Hz, *cis*-coupling) and of the carbonyl carbon atom ($^3J_{C,P}$ = 2.7 Hz, *trans* coupling).[7]

Oxidation of the λ^3-phosphorus of **4** to give the corresponding λ^5-phosphorus compounds was also possible.[18]



Scheme 6. Reagents and conditions: a) H_2O, acetone, 75% yield. b) $(Me_3SiO)_2$, CH_2Cl_2. c) S_8, CH_2Cl_2, 91%. d) RC≡CCO$_2$Me, 50 °C, 24 h (R=H: 61%; R = CO_2Me: 41%)

Treatment with bis(trimethylsilyl)peroxide gave the allenylphosphane oxide **11**. In spite of careful exclusion of moisture, the NMR spectra of the latter showed the presence of morpholine (ca. 5−6%), indicative of partial hydrolysis of the enamine function. The simultaneous presence of the resulting α,β-unsaturated ketone was not fully established by the NMR spectra, since most signals were covered by those of the allene, but was clearly shown by the expected molecular ion peaks in the mass spectra of **11**.

On the other hand, elemental sulfur did not only oxidize the P atom but also reacted with the nucleophilic enamine function, resulting in the formation of betaine **16**, which formed completely stable, bright ruby-red crystals. Reactions between enamines and S_8 have been known for some time,[19] and related dipolar iminium sulfides have been isolated in cases in which the positive charge was delocalized in a tetraalkylamidinium unit.[20] A similar betaine was postulated as an intermediate in reactions between push-pull substituted 1,1-diethoxyallenes and sulfur.[21]

The constitution and the double bond configuration of **16** were confirmed by an X-ray crystal structure determination (Figure 2). Notably, the π systems of the C=C and the $C=N^+$ bond are no longer in conjugation but are almost orthogonal to each other. Also interesting is the small bond angle C1−C2−S1 (106.1°), which may indicate some degree of attractive electrostatic interaction between the anionic sulfur and the cationic iminium function; however, no pyramidalization of the iminium carbon C1 is seen. On the other hand, steric repulsion with the substituents at the opposite end of the double bond is also likely to contribute to the angle deformation at C2, resulting in compression of angle C1−C2−S1 and widening of the two other bond angles.

Betaine **16** was found to undergo a dipolar [3+2] cycloaddition reaction with methyl propiolate, as well as with dimethyl acetylenedicarboxylate, to give the 5-benzylidene-4,5-dihydrothiophenes **17** and **18**, respectively (Scheme 6). The structure of **18** was also established by an X-ray crystal structure analysis (Figure 3). For **17**, an analogous structure

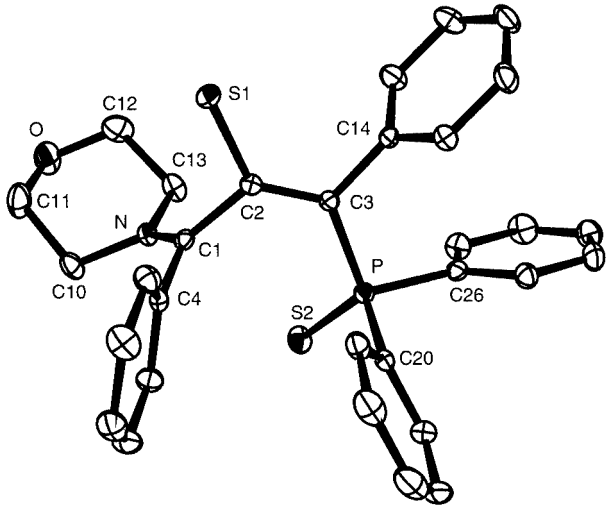


Figure 2. Structure of **16** in the crystal (ORTEP plot); ellipsoids of thermal vibration are shown at the 20% probability level; hydrogen atoms are not shown; selected bond lengths [Å] and angles [°]: C1−N 1.310(2), C1−C2 1.488(3), C2−C3 1.354(3), C3−P 1.803(2), C2−S1 1.715(2), P−S2 1.960(1); C1−C2−C3 126.4(2), C1−C2−S1 106.1(1), C3−C2−S1 127.4(1), C2−C3−P 123.5(1); torsion angles [°]: N−C1−C2−S1 83.1(2), C4−C1−C2−C3 82.6(2), C2−C3−P−S2 36.0(2)

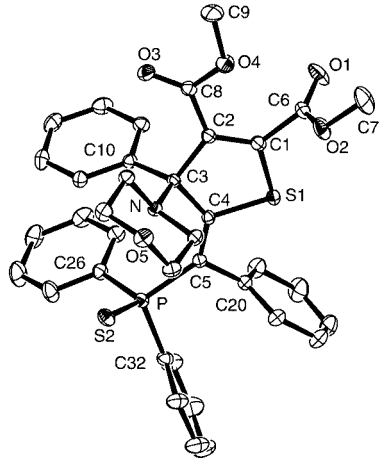


Figure 3. Structure of **18** in the crystal (ORTEP plot); ellipsoids of thermal vibration are shown at the 20% probability level; hydrogen atoms are not shown; selected bond lengths [Å] and angles [°]: C1−C2 1.332(5), C2−C3 1.535(5), C3−C4 1.566(5), C4−C5 1.353(5), C5−P 1.840(3), P−S2 1.949(1); C1−S1−C4 92.4(2), C3−C4−C5 134.1(3), S1−C4−C5 115.2(2), C4−C5−P 130.2(2), C4−C5−C20 116.2(3)

is assumed on the basis of the similar shifts of carbon atoms C-4 and C-5 in the dihydrothiophene ring and of the P,C-5 coupling constant. The orientation of the unsymmetrical dipolarophile is derived from the presumed polar character of the cycloaddition reaction; it is also in accordance with the observation of a $^5J_{H,P}$ coupling (0.9 Hz) through a W-shaped bond geometry. Other dipolarophiles, such as maleic anhydride, dimethyl fumarate and dimethyl maleate, did not react with **16** at 50 °C, while unspecific decomposition of the betaine set in around 80 °C.

The identification of allenes **4**, **5**, and **11** and their distinction from the isomeric propargyl compounds was readily achieved through their ^{13}C NMR spectra (Table 1). The chemical shifts of the central allenic carbon atom [$\delta(C^2)$] are diagnostic. They are very close to those of other fully substituted aminoallenes,[2b,3d] and they indicate that the shielding effect of the PR_2 groups on this carbon atom is small. Replacement of these substituents by an electron-withdrawing phosphoryl group results in the expected deshielding of the central allenic carbon atom, but again the effect is small (δ = 4.6 ppm for the change from **4** to **11**, for example). IR spectroscopy is not suited to identification of the allenic or propargyl reaction products. No C≡C stretching vibration was observed for **6** and **12**, and the C=C=C valence vibrations of the allenes, expected as weak and broad absorption(s) in the 1880−1920 cm^{-1} range,[2b,3d,18] were either too weak to be observed or coincided with overtones of the aromatic rings.

Table 1. Selected NMR spectroscopic data of (morpholinoallenyl)-phosphanes and -phosphoryl compounds, morpholino(Ph)C^3=C^2=C^1(Ph)R

Allene	R	$\delta(C^1)$ [ppm] ($^1J_{C,P}$ [Hz])	$\delta(C^2)$ [ppm] ($^2J_{C,P}$ [Hz])	δ(P) [ppm]
4	PPh_2	111.8 (19)	205.7 (−)	−7.1
5[a]	P(Ph)Pent	112.8 (22)	202.6 (−)	−19.1
		113.2 (22)	202.2 (−)	−19.9
11	$P(=O)Ph_2$	110.0 (101)	210.3 (5.3)	29.5

[a] Two diastereomers.

Conclusion

Propyne iminium salts are ambident electrophiles capable of reacting with phosphorus(III) nucleophiles either at the iminium function (C-1 attack) or at the β-position of the C≡C bond. The regioselectivity depends on both reaction partners. Both reaction modes give interesting products: C-1 attack allows the preparation of novel α-alkynyl-α-aminophosphonates, which may be of interest as bioisosters of non-natural α-amino acid esters, while the conjugate addition affords 3-aminoallenylphosphanes and -phosphane oxides, which constitute novel 1,3-bis(donor)- and push-pull-substituted allenes, respectively. This method for the preparation of phosphorus-substituted allenes is conceptually different from previous ones, which furnished allenylphosphanes from allenyl anions and phosphorus electrophiles,[18,22] and PO-substituted allenes from propargyl alcohols and chlorophosphanes followed by [2,3] rearrangement.[23] We have presented some examples of further transformations of the (3-morpholinoallenyl)phosphane **4**, which illustrate that selective functionalization of either the enamine or the (vinyl)phosphane functionality is possible. We have reported elsewhere that dialkylaminoallenes are converted thermally into condensed dihydroazepine derivatives.[3c] In the cases of **4**, **11**, and related allenes, thermal treatment results in either azepine or pyrrole derivatives.[15] These useful transformations will be reported in due course.

Experimental Section

General Remarks: Reactions were carried out in rigorously dried glassware and under argon. Solvents were dried by standard procedures and kept under argon. The petroleum ether used had a boiling point range of 30−60 °C. Column chromatography was performed under hydrostatic conditions on silica gel (Si, 60, 0.063−0.2 mm, Macherey−Nagel) with distilled eluents; for flash chromatography, pressurized nitrogen gas was applied. NMR spectra: Bruker AMX 500 (^{1}H: 500.14 MHz; ^{13}C: 125.77 MHz; ^{31}P: 202.48 MHz) and Bruker AC 200 (^{1}H: 200.13 MHz; ^{13}C: 50.32 MHz). $CDCl_3$ was used as the solvent for all spectra. The following references were applied: internal TMS for the proton spectra (δ = 0.00 ppm), the solvent signal for the ^{13}C NMR spectra [δ(*C*HCl_3) = 77.0 ppm], and external 85% H_3PO_4 (δ = 0.00 ppm) for the ^{31}P spectra. IR spectra: Perkin−Elmer IR 883 spectrometer. Mass spectra: Varian MAT 711 (FD) and Finnigan MAT SSQ 7000 (EI, FAB). Microanalyses: Elementar Vario EL, Division of Analytical Chemistry, University of Ulm. Melting points were determined in a Büchi apparatus according to Dr. Tottoli and are uncorrected.

The following compounds were prepared by literature methods: iminium salts **1a** and **1b**;[24] phosphane derivatives **2a**,[25] **2b**,[26], **2c**[27], **2d**,[28], and **2e**.[9a,29] Anhydrous lithium chloride was obtained by heating at 150 °C/0.04 mbar for 2 h.

(3-Morpholino-1,3-diphenyl-1,2-propadienyl)diphenylphosphane (4): A solution of salt **1a** (4.25 g, 10.0 mmol) and anhydrous lithium chloride (0.80 g, 18.9 mmol) in anhydrous THF (50 mL) was cooled to −78 °C. Diphenyl(trimethylsilyl)phosphane (**2a**, 2.58 g, 10 mmol) was added, and the mixture was brought to room temp. over 12 h, whereupon its color changed to black. The volatiles were evaporated, and the residue was triturated with pentane (30 mL) in an ultrasonic bath to remove any components of low polarity. The residue was then extracted with anhydrous toluene (3 × 30 mL); the extract was separated each time by filtration under argon. The combined toluene extracts were evaporated to dryness, and anhydrous ether (30 mL) was added. After a short time, allene **4** started to separate as a greenish-gray, microcrystalline solid, which could not be purified further because of its hydrolytic lability; yield: 3.64 g (79%), m.p. 122 °C. IR (KBr): ṽ = 1595 (m), 1488 (s), 1446 (s), 1434 (s), 1232 (s), 1116 (vs), 766 (vs), 745 (s), 695 (vs) cm^{-1}. ^{1}H NMR (500.14 MHz): δ = 2.32−2.45 (m, 4 H, NCH_2), 3.55−3.65 (m, 4 H, OCH_2), 7.15−7.40 (m, 18 H_{aryl}), 7.65−7.68 (m, 2 H_{aryl}) ppm. ^{13}C{^{1}H} NMR (125.77 MHz): δ = 50.8 (s, NCH_2), 66.9 (s, OCH_2), 111.8 (d, $^1J_{C,P}$ = 19 Hz, C-1$_{allene}$), 127.0−129.0 and 133.8−137.4 (C_{aryl}, NC=), 205.7 (s, C-2$_{allene}$) ppm. ^{31}P NMR: δ = −7.1 ppm. MS (EI, 70 eV): *m*/*z* (%) = 461 (2) [M$^+$], 276 (100) [M$^+$ − PPh_2]. $C_{31}H_{28}NOP$ (461.54): calcd. C 80.67, H 6.11, N 3.03; found C 79.29, H 6.60, N 2.77.

(3-Morpholino-1,3-diphenyl-1,2-propadienyl)(pentyl)phenylphosphane (5): The synthesis was performed as described for **4**, from iminium salt **1a** (2.44 g, 5.7 mmol), anhydrous lithium chloride (0.40 g, 9.4 mmol), and pentyl-phenyl(trimethylsilyl)phosphane (**2b**, 1.45 g, 5.7 mmol) in THF (50 mL). Allene **5** was obtained as a light-brown oil, which was not analytically pure but could not be purified further due to its hydrolytic lability; yield: 2.10 g (80%). IR (KBr): ṽ = 1666 (w), 1597 (m), 1488 (m), 1446 (s), 1299 (s), 1260 (s), 1233 (s), 1118 (vs), 762 (s), 744 (s), 697 (vs) cm^{-1}. ^{1}H NMR (500.14 MHz): δ = 0.82−2.00 (m, 11 H_{pentyl}), 2.66−2.85 (m, 4 H, NCH_2), 3.75−3.87 (m, 4 H, OCH_2), 7.15−7.85 (15 H_{aryl}) ppm. ^{13}C{^{1}H} NMR (125.77 MHz): δ (major/minor diastereomer) = 13.68/13.74 (s, C-5$_{pentyl}$), 21.99/22.06 (s, C-4$_{pentyl}$), 25.33−25.66, 27.83−28.03, 32.86−33.22 (2 d in all cases, C-1,-2,-3$_{pentyl}$), 51.4/51.1 (s, NCH_2), 66.73 (s, OCH_2), 112.8/113.2 (both d, $^1J_{C,P}$ = 22 Hz, C-1$_{allene}$), 126.6−137.2 (C_{aryl}, NC=), 202.6/202.2 (C-2$_{allene}$) ppm. ^{31}P NMR: δ = −19.1 (major), −19.9 (minor) ppm. MS (FD): *m*/*z* (%) = 455 (100) [M$^+$]. $C_{30}H_{34}NOP$ (455.58).

Diethyl(1-morpholino-1,3-diphenyl-2-propynyl)phosphane (6): A solution of iminium salt **1a** (3.40 g, 8.0 mmol) and anhydrous lithium chloride (0.80 g, 18.9 mmol) in THF (30 mL) was cooled to −78 °C. Diethyl(trimethylsilyl)phosphane (**2c**, 1.23 g, 8.0 mmol) was added, and the mixture was brought to room temp. over 12 h. The volatiles were evaporated, and ether (150 mL) was added to the residue. After extraction with two portions of water (100 and 50 mL), the organic phase was dried ($CaCl_2$), and the solvent was evaporated. The residue was recrystallized from cyclohexane/ethyl acetate to give clear, colorless crystals; yield: 2.05 g (70%); m.p. 112 °C. IR (KBr): ṽ = 1597 (m), 1485 (s), 1444 (s), 1263 (s), 1122 (s), 1112 (vs), 921 (s), 760 (s), 705 (s) cm^{-1}. ^{1}H NMR (500.14 MHz): δ = 0.83−1.21 (m, 9 H, PCH_2CH_3, PCH_2, PCH), 1.62−1.64 (m, 1 H, PCH), 2.61 (m$_c$, 2 H, NCH_2), 2.97 (m$_c$, 2 H, NCH_2), 3.70−3.75 (m, 4 H, OCH_2), 7.20−7.67 (10 H_{aryl}) ppm. ^{13}C{^{1}H} NMR (125.77 MHz): δ = 10.3 (d, CH_3), 11.1 (d, CH_3), 18.1 (d, *J* = 18.9 Hz, PCH_2), 19.3 (d, *J* = 17.6 Hz, PCH_2), 49.4 (d, $^3J_{C,P}$ = 11. 3 Hz, NCH_2), 67.4 (s, OCH_2), 68.6 (d, $^1J_{C,P}$ = 12.6 Hz, C-1), 86.2 (d, $^2J_{C,P}$ = 7.6 Hz, C-2), 91.0 (d, $^3J_{C,P}$ = 2.5 Hz, C-3), 123.1, 127.0, 128.1, 128.3, 131.7, 138.2, 138.3 (C_{aryl}) ppm. ^{31}P NMR: δ = 9.4 ppm. MS (FD): *m*/*z* (%) = 365 (3) [M$^+$], 276 (100) [M$^+$ − PEt_2]. $C_{23}H_{28}NOP$ (365.45): calcd. C 75.59, H 7.72, N 3.83; found C 75.92, H 7.77, N 3.73.

[(1*E*)-3-Morpholino-1-phenyl-1,3-butadienyl]diphenylphosphane (8): The synthesis was performed as described for **4**, from iminium salt **1b** (1.82 g, 5.0 mmol), anhydrous lithium chloride (0.40 g, 9.4 mmol), and phosphane **2a** (1.29 g, 5.0 mmol) in THF (50 mL). A light brown oil was obtained; yield: 1.26 g (63%). IR (KBr): ṽ = 1650 (m), 1585 (m), 1425 (m), 1100 (m) cm^{-1}. ^{1}H NMR (500.14 MHz): δ = 2.61 (m$_c$, 4 H, NCH_2), 3.21 (m$_c$, 4 H, OCH_2), 3.93 (s, 1 H, 4-H^1), 3.97 (s, 1 H, 4-H^2), 5.91 (d, $^3J_{H,P}$ = 7.4 Hz, 1 H, 2-H), 7.0−7.6 (15 H_{aryl}) ppm. ^{13}C{^{1}H} NMR (125.77 MHz): δ = 48.5 (s, NCH_2), 66.0 (s, OCH_2), 92.2 (s, C-4), 118.7−143.2 (C_{aryl}, C-1,-2), 152.0 (d, $^3J_{C,P}$ = 4.8 Hz, C-3) ppm. ^{31}P NMR: δ = 4.4 ppm. $C_{26}H_{26}NOP$ (399.47): calcd. C 78.17, H 6.56, N 3.51; found C 78.55, H 6.70, N 3.18.

(2*E*)-4-Morpholino-1,3,4,6-tetraphenylhex-2-en-5-yn-1-one (10): Potassium (0.20 g, 5.1 g-atom) and chloro(diphenyl)phosphane (1.10 g, 5.0 mmol) were added successively to anhydrous THF (200 mL), and the mixture was heated at reflux until the metal had disappeared (3 h). The solution was cooled to −78 °C and solid iminium salt **1a** (2.13 g, 5.0 mmol) was added from a wide-bore funnel. The mixture was brought to room temp. over 12 h, the solvent was removed at 14 mbar, and the residue was subjected to flash column chromatography (silica gel, eluent: cyclohexane/ethyl acetate, 5:1). An off-white solid was isolated from the second fraction and was recrystallized from cyclohexane to give **10** (0.20 g, 17%), m.p. 168 °C. IR (KBr): ṽ = 1644, 1264, 1113, 694 cm^{-1}. ^{1}H NMR (500.14 MHz): δ = 2.62−2.74 (m, broad, 2 H, NCH_2), 2.88−3.05 (m, 2 H, NCH_2), 3.87 (m$_c$, 4 H, OCH_2), 6.66 (d, *J* = 8.4 Hz, 2 H_{aryl}), 7.03−7.77 (several m, 18 H_{aryl}), 7.71 (s, 1 H, H_{olefin}). ^{13}C NMR (125.77 MHz): δ = 49.4 (NCH_2), 67.4 (OCH_2), 74.0 (C-4), 84.9 and 92.5 (C≡C), 122.6, 126.2−129.4, 131.7, 132.7, 137.0, 138.2, 139.0, 154.1, 193.3 (C=O). MS (FAB, *p*-nitrobenzyl alcohol): *m*/*z* (%) = 484 (6) [M$^+$], 397 (19), 276 (100). $C_{34}H_{29}NO_2$ (483.61): calcd. C 84.44, H 6.04, N 2.90; found C 82.94, H 5.98, N 2.60.

(3-Morpholino-1,3-diphenyl-1,2-propadienyl)diphenylphosphane Oxide (11). Method A: The synthesis was performed as described for **4** from iminium salt **1a** (4.25 g, 10.0 mmol), anhydrous lithium chloride (0.80 g, 18.9 mmol), and diphenyl(trimethylsilyloxy)phosphane (**2d**, 2.74 g, 10.0 mmol) in THF (50 mL). After evaporation of the volatiles, a mixture of allene **11** and of lithium trifluoromethanesulfonate was obtained. This could not be completely separated by extraction, but was suited for further transformations of **11.**

Method B: Bis(trimethylsilyl)peroxide (0.89 g, 5.0 mmol) was added to a solution of allene **4** (2.31 g, 5.0 mmol) in CH_2Cl_2 (10 mL). After the mixture had been stirred for 12 h, the volatiles were evaporated at 14 mbar. The pale yellow, solid residue consisted of allene **11** contaminated with a compound that is likely to be the hydrolysis product (3-oxo-1,3-diphenyl-1-propenyl)diphenylphosphane oxide (ca. 6%) [$^{13}C\{^1H\}$ NMR: δ = 140.2 (d, $^2J_{C,P}$ = 8.4 Hz), 193.3 (d, $^3J_{C,P}$ = 17.1 Hz, C=O) ppm. ^{31}P NMR: δ = 29.0 ppm]. Further purification of **11** was not possible, due to its hydrolytic lability. ^1H NMR (500.14 MHz): δ = 2.40−2.58 (m, 4 H, NCH_2), 3.55−3.65 (m, 4 H, OCH_2), 7.16−7.72 (20 H_{aryl}) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz): δ = 50.3 (s, NCH_2), 66.4 (s, OCH_2), 110.0 (d, $^1J_{C,P}$ = 100.6 Hz, C-1_{allene}), 127.0−133.1 (C_{aryl}, NC=), 210.3 (d, $^2J_{C,P}$ = 5.3 Hz, C-2_{allene}) ppm. ^{31}P NMR: δ = 29.5 ppm.

Diethyl (1-Morpholino-1,3-diphenyl-2-propynyl)phosphonate (12). From 1a and 2e (Method A): The synthesis was carried out as described above for **6**, from iminium salt **1a** (2.12 g, 5.0 mmol), lithium chloride (0.40 g, 9.4 mmol), and diethoxy(trimethylsilyloxy)-phosphane (**2e**, 1.05 g, 5.0 mmol). After crystallization from cyclohexane/ethyl acetate, clear, colorless crystals were obtained (1.55 g, 75% yield); m.p. 132−133 °C.

From 1a and 2f (Method B): Diethyl phosphite (0.69 g, 5.0 mmol) and ethyldiisopropylamine (0.65 g, 5.0 mmol) were added to a solution of salt **1a** (2.12 g, 5.0 mmol) in dichloromethane (30 mL). After stirring at room temp. for 12 h, the mixture was extracted twice with water (100 and 50 mL). The organic layer was dried ($CaCl_2$), the solvent was evaporated, and the residue was recrystallized as in method A; yield: 1.42 g (69%). IR (KBr): $\tilde{\nu}$ = 1486 (m), 1445 (m), 1245 (s, P=O), 1114 (s), 1055 (s), 1022 (vs, P−O−C), 960 (s), 698 (s) cm^{-1}. ^1H NMR (200.13 MHz): δ = 1.11 and 1.29 (each t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 2.50−2.65 and 2.90−3.10 (2 m, 4 H, NCH_2), 3.40−4.25 (3 m, 4 H, $POCH_2$), 3.75 (pseudo-t, 4 H, morpholine−OCH_2), 7.25−7.40 (m, 6 H_{aryl}), 7.55−7.65 (m, 2 H_{aryl}), 7.95−8.05 (m, 2 H_{aryl}) ppm. $^{13}C\{^1H\}$ NMR (50.32 MHz): δ = 15.75 (d, $^3J_{C,P}$ = 4.5 Hz, CH_3), 15.97 (d, $^3J_{C,P}$ = 4.9 Hz), 48.9 (d, $^3J_{C,P}$ = 7.0 Hz, NCH_2), 63.39 (d, $^2J_{C,P}$ = 8.8 Hz, $POCH_2$), 63.56 (d, $^2J_{C,P}$ = 7.7 Hz, $POCH_2$), 66.8 (s, OCH_2), 69.1 (d, $^1J_{C,P}$ = 162 Hz, C-1), 82.0 (d, $^2J_{C,P}$ = 4.6 Hz, C-2), 91.2 (d, $^3J_{C,P}$ = 9.3 Hz, C-3), 122.1, 127.6, 127.9, 128.0, 128.2, 128.9, 131.5, 136.1 (d) (C_{aryl}) ppm. ^{31}P NMR: δ = 18.1 ppm. $C_{23}H_{28}NO_4P$ (413.45): calcd. C 66.82, H 6.82, N 3.39; found C 66.81, H 6.84, N 3.34.

(2*E*)-3-(Diphenylphosphanyl)-1,3-diphenyl-2-propen-1-one (15): Allene **4** (2.54 g, 5.5 mmol) was dissolved in acetone (30 mL), and water (1 mL) was added. The mixture was stirred for 12 h under argon. Evaporation of the solvent at 15 mbar and of other volatile components at 0.01 mbar, followed by recrystallization from cyclohexane/ethyl acetate, afforded 1.62 g (75%) of **15** as yellow crystals, m.p. 126−127 °C. IR (KBr): $\tilde{\nu}$ = 1662 (s, C=O), 1435 (m), 1228 (s), 746 (s), 695 (vs) cm^{-1}. ^1H NMR (500.14 MHz): δ = 6.25 (d, $^3J_{H,P}$ = 3.5 Hz, 2-H), 6.98−7.61 (20 H_{aryl}) ppm. ^{13}C NMR (125.77 MHz): δ = 127.9−134.6 (C_{aryl}, C-2), 137.4 (s), 138.9 (d, $J_{C,P}$ = 20.1 Hz), 155.5 (d, $J_{C,P}$ = 25.1 Hz, C-3), 193.7 (d, $^3J_{C,P}$ = 2.7 Hz, C-1) ppm. ^{31}P NMR: δ = 4.3 ppm. $C_{27}H_{21}OP$ (392.44): calcd. C 82.64, H 5.39; found C 82.55, H 5.60.

(*E*)-1-(Diphenylthiophosphoryl)-3-(1,4-oxazinan-4-ium-4-ylidene)-1,3-diphenyl-1-propene-2-thiolate (16): Allene **4** (4.62 g, 10.0 mmol) was dissolved in dichloromethane (50 mL), and elemental sulfur (0.64 g, 20.0 g-atom, carefully dried over P_4O_{10}) was added with stirring. The solution quickly became orange-colored. After 2 h the solvent was removed, and acetonitrile (20 mL) was added to the residue. Betaine **16** separated as a microcrystalline, orange solid. Recrystallization from a dichloromethane solution with a surface layer of pentane gave well shaped, bright ruby red crystals; yield: 4.78 g (91%), m.p. 180 °C (dec.). IR (KBr): $\tilde{\nu}$ = 1596 (s), 1508 (s), 1436 (s), 1114 (s), 1100 (s), 711 (vs), 694 (vs) cm^{-1}. ^1H NMR (500.14 MHz): δ = 3.70−4.40 (m, 8 H, NCH_2CH_2O), 6.77 (d, *J* = 6.7 Hz, 2 H_{aryl}), 6.90−7.32 (m, 16 H_{aryl}), 8.23 (d, *J* = 7.9 Hz, 2 H_{aryl}) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz): δ = 52.4, 53.4 (s, NCH_2), 64.7, 65.0 (s, OCH_2), 123.2−132.5 (C_{aryl}), 139.1 (d, *J* = 8.8 Hz), 167.7 (d, *J* = 9.7 Hz), 173.3 (C=N^+) ppm. ^{31}P NMR: δ = 39.8 ppm. MS (FD): *m*/*z* = 525 [M^+]. $C_{31}H_{28}NOPS_2$ (525.66): calcd. C 70.83, H 5.37, N 2.66; found C 70.87, H 5.35, N 2.67.

Methyl 5-[(*E*)-1-(Diphenylthiophosphoryl)-1-phenylmethylidene]-4-morpholino-4-phenyl-4,5-dihydrothiophene-3-carboxylate (17): A solution of betaine **16** (2.62 g, 5.0 mmol) and methyl propiolate (0.42 g, 5.0 mmol) in dichloromethane (20 mL) was placed in a thick-walled Schlenk tube and heated at 50 °C for 24 h. The solvent was evaporated, and the residue was subjected to column chromatography (250 g of silica gel; eluent: cyclohexane/ethyl acetate, 1:1). After recrystallization from the same solvent mixture, 1.85 g (61%) of **17** was obtained as a yellow solid, which started to decompose above 160 °C and melted at 201 °C. IR (KBr): $\tilde{\nu}$ = 1714 (vs, C=O), 1573 (m), 1435 (m), 1285 (s), 1206 (s), 1113 (s), 694 (s) cm^{-1}. ^1H NMR (500.14 MHz): δ = 2.77 and 2.97 (2 m_c, 4 H, NCH_2), 3.51 (s, 3 H, OCH_3), 3.98 and 4.19 (2 m_c, 4 H, OCH_2), 5.26 (d, $^5J_{H,P}$ = 0.9 Hz, 1 H, 2-H), 6.70−7.37 (18 H_{aryl}), 7.63 (d, *J* = 6.0 Hz, 2 H_{aryl}) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz): δ = 49.8 (s, NCH_2), 51.4 (s, OCH_3), 67.0 (s, OCH_2), 82.2 (s, C-4), 126.7−143.5 (C_{aryl}, 3 C_{olefin}), 162.3 (C=O), 165.3 (d, $^2J_{C,P}$ = 9.8 Hz, C-5) ppm. ^{31}P NMR: δ = 40.5 ppm. MS (EI, 70 eV): *m*/*z* (%) = 609 (8) [M^+], 524 (84) [$M^+ - C_4H_7NO$], 392 (43) [$M^+ - Ph_2PS$]. $C_{35}H_{32}NO_3PS_2$ (609.74): calcd. C 68.94, H 5.29, N 2.30; found C 68.77, H 5.40, N 2.21.

Dimethyl 5-[(*E*)-1-(Diphenylthiophosphoryl)-1-phenylmethylidene]-4-morpholino-4-phenyl-4,5-dihydrothiophene-2,3-dicarboxylate (18): A solution of betaine **16** (2.62 g, 5.0 mmol) and dimethyl acetylenedicarboxylate (0.71 g, 5.0 mmol) in dichloromethane (20 mL) was placed in a thick-walled Schlenk tube and heated at 50 °C for 24 h. The solvent was evaporated, the residue was dissolved in the minimum amount of ethyl acetate, and cyclohexane was added until the solution became turbid. After some time, solid **18** separated as the cyclohexane solvate, which strongly retained the solvate molecules. When a chloroform solution of this material was slowly concentrated, well shaped yellow crystals of a chloroform solvate were obtained; after being kept at 0.01 mbar/ 20 °C they had the composition **18**·$CHCl_3$; yield: 1.61 g (41%), m.p. 134 °C. IR (KBr): $\tilde{\nu}$ = 1731 (vs), 1613 (m), 1435 (s), 1276 (vs), 1247 (vs), 1113 (s), 704 (m), 693 (m) cm^{-1}. ^1H NMR (500.14 MHz): δ = 2.95−3.10 (2 m, 4 H, NCH_2), 3.52 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3), 4.01 and 4.18 (2 m_c, 4 H, OCH_2), 6.68−7.33 (18 H_{aryl}), 7.74 (d, *J* = 7.5 Hz, 2 H_{aryl}) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz): δ = 49.1 (s, NCH_2), 52.0 and 52.8 (OCH_3), 66.7 (s, OCH_2), 85.4 (s, C-4), 126.7−143.1 (C_{aryl}, 3 C_{olefin}), 161.8, 163.3 (C=O), 162.7 (d, $^2J_{C,P}$ = 10.2 Hz, C-

Table 2. Data for X-ray diffraction structure determination of compounds **10**, **16**, and **18**

	10	**16**	**18**
Empirical formula	$C_{34}H_{29}NO_2$	$C_{31}H_{28}NOPS_2$	$C_{37}H_{34}NO_5PS_2 \times 1.8\ CHCl_3$ [a]
Molecular mass	483.58	525.69	667.77 (882.60)
Temperature [K]	293(2)	293(2)	293(2)
Crystal size [mm]	0.38 × 0.30 × 0.15	0.70 × 0.60 × 0.60	0.54 × 0.38 × 0.27
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a [Å]	12.977(2)	12.689(4)	12.343(2)
b [Å]	10.074(1)	16.363(5)	12.598(2)
c [Å]	20.638(4)	14.201(4)	15.043(3)
α [°]	90	90	74.14(2)
β [°]	91.79(2)	114.05(2)	87.90(2)
γ [°]	90	90	68.68(2)
V [Å^3]	2696.6(8)	2692.7(1)	2091.0(7)
Z	4	8	2
$\rho_{calcd.}$ [g cm^{-3}]	1.191	1.297	1.402
μ(Mo-K_α) [mm^{-1}]	0.073	0.24	0.55
θ range [°]	1.88−23.53	1.82−24.27	1.78−24.15
Index ranges	$-14 \le h \le 14$	$-14 \le h \le 13$	$-14 \le h \le 13$
	$-11 \le k \le 11$	$0 \le k \le 18$	$-14 \le k \le 14$
	$-23 \le l \le 23$	$0 \le l \le 16$	$-17 \le l \le 17$
Reflections collected	16125	23229	13464
Independent reflections (R_{int})	4006 (0.0592)	4258 (0.0501)	6232 (0.0333)
Completeness of data set [%]	100	97.9	93.2
Data/restraints/parameters	4006/ 0/334	4258/ 0/349	6232/0/491
Goodness-of-fit on F^2	0.810	0.821	1.050
Final R indices [$I > 2\sigma(I)$]; $R1$, $wR2$	0.0382, 0.0826	0.0296, 0.0582	0.0570, 0.1658
R indices (all data); $R1$, $wR2$	0.0782, 0.0918	0.0536, 0.0624	0.0749, 0.1790
Largest diff. peak and hole [e·Å^{-3}]	0.10, −0.11	0.16, −0.21	0.83, −0.54

[a] One of the two $CHCl_3$ solvate molecules per formula unit showed rather high displacement ellipsoids, and the highest residual electron density was found in this region. The occupancy factor of this molecule was refined and finally fixed at 0.80.

5) ppm. ^{31}P NMR: δ = 40.8 ppm. MS (EI, 70 eV): *m/z* (%) = 667 (50) [M$^+$], 608 (82) [M$^+$ − CO_2Me], 582 (97) [M$^+$ − C_4H_7NO], 450 (62) [M$^+$ − Ph_2PS], 418 (100). $C_{37}H_{34}NO_5PS_2{\cdot}CHCl_3$ (787.15): calcd. C 57.98, H 4.48, N 1.78; found C 58.37, H 4.58, N 1.89.

X-ray Crystallographic Study:[30] Single crystals of **10** were obtained by crystallization from an acetonitrile solution, those of **16** from a CH_2Cl_2 solution with a layer of pentane, and those of **18** from a $CHCl_3$ solution with a layer of petroleum ether. Data collection was carried out on a Stoe IPDS instrument by use of monochromatized Mo-K_α radiation. The structures were solved with direct methods and refined by a full-matrix, least-squares method (G. M. Sheldrick, SHELX-97, University of Göttingen, **1997**). Molecule plots were made with ORTEP-3 for Windows (L. J. Farrugia, University of Glasgow, **1998**). Crystallographic data and details of the refinement for the three structures are given in Table 2.

Acknowledgments

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