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Synthesis and Some Chemical Properties of a 1,2$\lambda^3\sigma^3$-Thiaphosphirane

Kostiantyn V. Turcheniuk,[a] Alexander B. Rozhenko,[b,c] and Igor V. Shevchenko*[a]

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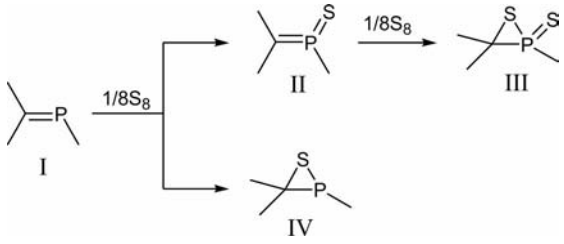
A rare example of the addition of sulfur to a phosphaalkene double bond leading to 1,2λ^3,σ^3-thiaphosphirane **4** is described. The relative accessibility of this compound has allowed the study of some of the chemical properties of the thiaphosphirane ring. The thermodynamic stability of 1,2λ^3,σ^3-thiaphosphiranes compared with λ^5,σ^3-phosphoranes has been studied by DFT calculations.

Introduction

It is known that phosphaalkenes **I** can add two atoms of sulfur with the formation of λ^5,σ^4-thiaphosphiranes **III** (Scheme 1), that is, a CPS three-membered ring system.[1] The number of known examples is limited to 15 and the mechanism of the reaction is not quite clear yet.[2] The first sulfur atom does not add to the P=C bond of the phosphaalkenes but to the two-coordinate phosphorus atom to give reactive and usually rather unstable intermediates λ^5,σ^3-phosphoranes **II**. The formation of the thiaphosphirane cyclic system results from the addition of the second sulfur atom to the double-bond P=C π system of compounds **II**. The presence of a completely oxidized phosphorus atom reduces the value of these compounds as starting materials for investigating the properties of the CPS cycle and for their possible use in further chemical transformations. Despite some isolated instances of the reduction of compounds **III** to 1,2λ^3,σ^3-thiaphosphiranes **IV** or isomerization of compounds **II**[1j,1k,1l] to **IV**, the latter remain difficult to access and unexplored compounds.

There are only three examples known of the interaction of phosphaalkenes **I** with sulfur leading to the formation of 1,2λ^3,σ^3-thiaphosphiranes **IV**.[3] Clearly, this results from the addition of sulfur to the P=C bond. The intermediate formation of λ^5,σ^3-phosphoranes **II** and their subsequent isomerization were not detected in these cases. The structural isomers **II** and **IV** are easily distinguishable by ^{31}P NMR spectroscopy as their chemical shift values differ significantly.



Scheme 1.

In this paper we describe one more rare example of the addition of sulfur to the phosphaalkene double bond leading to 1,2λ^3,σ^3-thiaphosphirane **4**. The relative accessibility of this compound allowed the study of some of the chemical properties of the thiaphosphirane ring.

We have also carried out quantum chemical investigations of **4a** as a model system, as well as the parent compound **4b** and compared them with their λ^5,σ^3 structural isomers (**3a** and **3b**, respectively).

Results and Discussion

We found that phosphaalkene **2** adds sulfur to the P=C bond with the retention of the three-valent state of the phosphorus atom and the formation of 1,2λ^3,σ^3-thiaphosphirane **4**. Phosphaalkene **2** (Scheme 2) can be almost quantitatively obtained by the dehydrochlorination of the appropriate chlorophosphane **1** with 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU). This reaction proceeds very easily and immediately after addition of the base the ^{31}P NMR spectrum displays only two doublets, one of which is at a very high frequency (+305 ppm), which is characteristic of a two-coordinate phosphorus atom. The addition of an equivalent amount of sulfur to the freshly obtained phosphaalkene instantly and quantitatively gave thiaphosphirane **4** (Scheme 2). The ^{31}P NMR spectrum of the solution of compound **4** thus obtained showed only two intense doublets at 66.3 and –36.5 ppm ($^2J_{P,P}$ = 43 Hz). The low-fre-

[a] Institute of Bioorganic Chemistry and Petrochemistry of NAS of Ukraine,
Murmanskaya str. 1, 02660 Kiev, Ukraine
Fax: +38-044-5732552
E-mail: igorshevchenko@yahoo.com
[b] Institute of Organic Chemistry of NAS of Ukraine,
Murmanskaya str. 5, 02660 Kiev, Ukraine
[c] Fakultät für Chemie der Universität Bielefeld,
Postfach 10 01 31, 33501 Bielefeld, Germany
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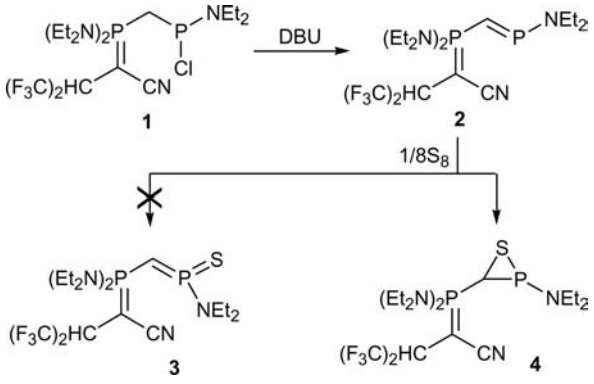
quency signal (–36.5 ppm) corresponds to the phosphorus in the thiaphosphirane ring and not to the λ⁵ phosphorus atom of the isomeric opened form **3**, the chemical shift of which should exceed +150 ppm. In addition to this, the P–C–P carbon atoms of the two isomers exist in different hybridized forms and thus have easily distinguishable chemical shifts. The ^{13}C NMR spectrum of the obtained compound displayed a doublet of doublets at δ = 22.7 ppm ($^1J_{P1,C}$ = 108 Hz, $^1J_{P2,C}$ = 60 Hz), which can be unambiguously assigned to the sp³-hybridized carbon of thiaphosphirane **4**. It is interesting that the APCI mass spectrum of this compound displays together with the mass peak at *m*/*z* = 513 $[M + H]^+$ only one very intense signal at *m*/*z* = 440 resulting from the elimination of diethylamine $[(M – Et_2NH) + H]^+$. This fragment is the protonated form of either the appropriate thiaphosphirene R-CPS containing an unsaturated three-membered cycle or the isomeric noncyclic sulfurated phosphaalkyne R–C≡P=S [R = $(CF_3)_2$-CHC(CN)=P$(NEt_2)_2$]. Formally, both structures can be considered as the products of the addition of sulfur to the phosphaalkyne triple bond C≡P. The possible formation of analogous structures as intermediates has previously been supposed by Märkl and Hölzl.[4]



Scheme 2.

Our DFT (B3LYP/6-31+G**) calculations confirmed this conclusion. The calculations showed λ³-thiaphosphirane **4a** (R = NMe_2; Figure 1) to be favoured more than the alternative phosphorane **3a** by 4.7 (4.1) kcal/mol (here and elsewhere the value in parentheses refers to the RIJCOSX-B3LYP/TZVP level of theory, see Calculations section). In addition, the values of the chemical shifts calculated for the λ³,σ³ and λ⁵,σ³ phosphorus atoms in **4a** and **3a** are –41.2 and +239.8 ppm, respectively (see the Supporting Information for details). Similarly, the calculated δ_C value for **4a** (δ = 21.1 ppm) agrees better with the experimental magnitude (δ = 22.7 ppm) than that predicted for **3a** (δ = 62.3 ppm)).

The reactivity of the phosphaalkene P=C unit with sulfur should be controlled both by electronic and steric factors. Analysis of all the known λ⁵-phosphoranes **II** and thiaphosphiranes **IV** allows one to suppose that less sterically demanding substituents at the phosphorus atom promote the formation of the thiaphosphirane CPS ring. In thiaphosphirane **4** the diethylamino group at the phosphorus atom is

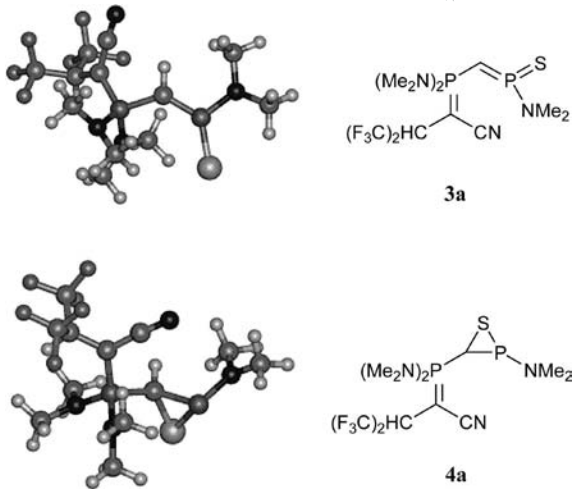
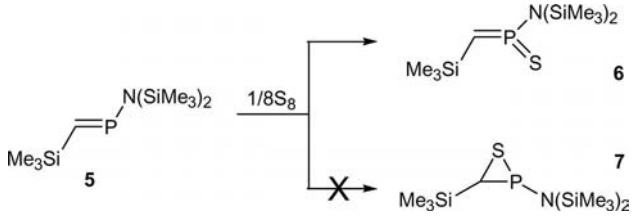


Figure 1. VMD presentation of the optimized (B3LYP/6-311++G**) structures of **3a** and **4a**.

smaller than the corresponding substituent in all known λ⁵-phosphoranes **II**. As an example, for comparison, we performed calculations on λ⁵-phosphorane **6**, experimentally obtained by Niecke and Wildbredt by the sulfuration of phosphaalkene **5**[1a] (Scheme 3). This compound, which features a more bulky substituent at the phosphorus atom, was found to be 0.5 (1.0) kcal/mol more stable than the alternative thiaphosphirane **7**.



Scheme 3.

On the other hand, our calculations on the parent thiaphosphirane **4b** (B3LYP/6-31+G**) confirmed that reducing the substituent bulk shows the opposite tendency. This compound is 9.1 kcal/mol more stable than the isomeric phosphorane **3b**.

There are two known examples of mutual transformation between isomers **II** and **IV**.[1j,1k] λ⁵,σ³-Phosphoranes **II** isomerize into λ³,σ³-thiaphosphiranes **IV** under UV irradiation, whereas the reverse process was observed upon heating. Thiaphosphirane **4** does not transform into isomer **3** either on heating or on exposure to a mercury vapour lamp in a solution of dichloromethane or toluene. The heating caused only fast decomposition into fluoro derivative **10**. The mechanism of the decomposition involves the reaction of **4** with HF, which is eliminated from the hexafluoroisopropyl fragment of another molecule of **4**. The process is similar to the decomposition of other such systems.[5,6]

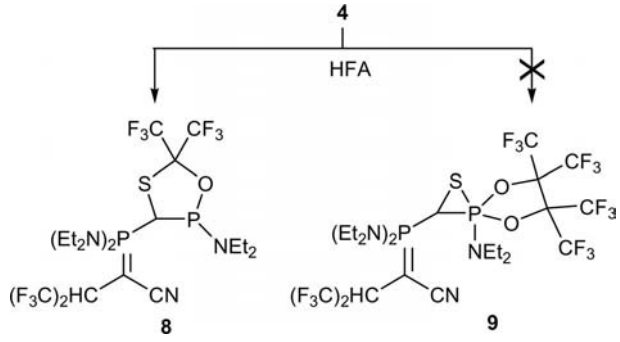
The relative simplicity of the synthesis of thiaphosphirane **4** allowed us to study some of its chemical properties. As the three-valent phosphorus atom in **4** is not substituted by strong electron-withdrawing groups one could expect this compound to be prone to oxidation. However, this did not turn out to be the case. For example, unlike formally five-valent structural isomers **II**, thiaphosphirane **4** is absolutely inert to sulfur and not even traces of the corresponding thioxo-thiaphosphirane of type **III** were detected in a reaction mixture after long contact with sulfur. This circumstance has already been mentioned for two of the thiaphosphiranes described previously.[3a,3b] Compound **4** does not form phosphonium salts with alkyl halides either. For instance, no reaction occurs with an excess of MeI at room temperature. Thiaphosphirane **4** is rather resistant even to a strong electrophile like tetrachloro-*o*-benzoquinone (TOB). The addition of 1 equiv. of TOB to a solution of **4** in toluene did not cause any changes in the ^{31}P NMR spectrum. After 24 h it showed a rather complicated mixture, with only low-intensity (about 10% of the total intensity) signals (d, δ = –21.8 ppm; d, δ = 59.2 ppm; $^2J_{PP}$ = 51 Hz), which could be attributed to the corresponding spirophosphorane. Taking into account the fact that **4** spontaneously decomposes in solution over 2 days, one can suppose that TOB reacts probably more readily with the decomposition products than with thiaphosphirane **4** itself.

The stability of thiaphosphirane **4** towards oxidation makes it different from the structurally similar non-cyclic thioamidophosphonites[7] and is probably accounted for by the peculiarity of the electronic structure of the CPS ring.

Hexafluoroacetone (HFA) is also a strong electrophile. Analogously to tetrachloro-*o*-benzoquinone, it readily oxidizes three-valent phosphorus compounds to give cyclic phosphoranes. However, with thiaphosphirane **4**, TOB and HFA turned out to be different. Unlike TOB, hexafluoroacetone reacts with **4** very easily, however, the expected oxidation of the phosphorus atom with the formation of spirophosphorane **9** does not occur. Only 1 equiv. of HFA reacts with **4** to cleave the P–S bond of the three-membered ring. This leads to the expansion of the ring and the formation of 1,4,2λ^3-oxathiaphospholane **8** (Scheme 4), which represents a new type of heterocyclic system. The ^{31}P NMR signal at δ = 165.7 ppm can only be assigned to the three-valent endocyclic phosphorus atom. This compound turned out to be unusually stable to oxidation. It does not react with HFA and is stable towards sulfur and oxygen.

The molecular structure of **8** was established by single-crystal X-ray analysis (Figure 2). The unusual chemical behaviour of **8** is accounted for by the fact that the lone-pair of the λ^3 P atom is shielded by the bulky hexafluoroisopropyl group. The five-membered heterocyclic ring has a distorted envelope conformation with the C1 atom in the flap position.

It has already been mentioned above that thiaphosphirane **4** decomposes slowly in solution at room temperature. This process is accounted for by the slow elimination of HF from the hexafluoroisopropyl group at the negatively charged ylidic carbon atom which then opens the thiaphosphirane ring to give fluorophosphonate **10**.[6]. The opening of the thiaphosphirane ring and the formation of **10** was also observed after addition of $Et_3N{\cdot}3HF$ to **4** (Scheme 5).



Scheme 4.

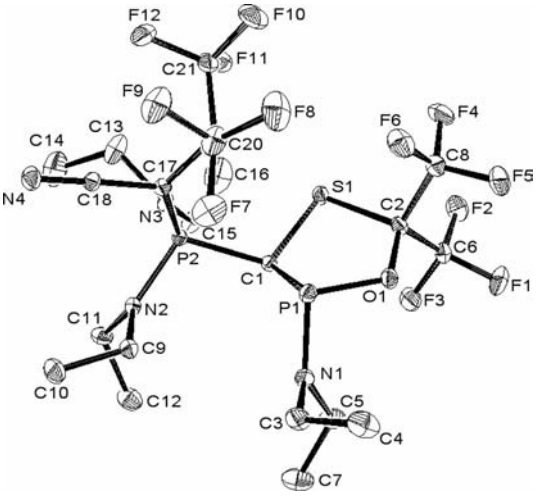
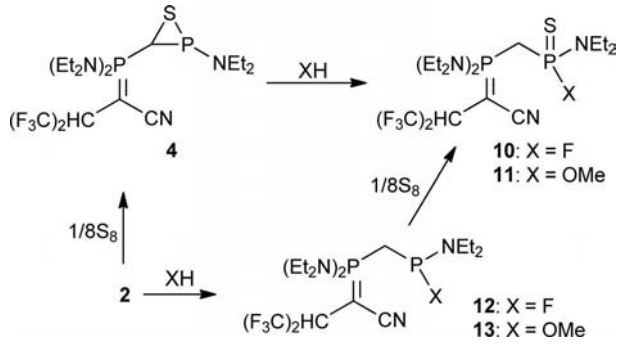


Figure 2. ORTEP drawing of **8** (ellipsoids drawn at the 20% probability level). Selected bond lengths [Å] and angles [°]: P1–C1 1.879, P1–O1 1.701, O1–C2 1.376, C2–S1 1.827, S1–C1 1.806, P2–C1 1.856, P1–N1 1.622, P2–C17 1.698; C1–S1–C2 95.80, S1–C1–P1 105.28, C1–P1–O1 92.53, P1–O1–C2 119.91, O1–C2–S1 111.53.



Scheme 5.

One could suppose that HCl would react with thiaphosphirane **4** analogously. However, addition of a toluene solution of HCl to **4** did not give the expected chloro derivative but led to slow decomposition of the starting compound and the formation of a complex reaction mixture. In contrast to HCl, the addition of 1 equiv. of methanol neatly

and quantitatively converted the thiaphosphirane into phosphonate **11**. Compounds **10** and **11** were independently obtained from phosphaalkene **2** and XH (X = MeO, F) by the intermediate formation of three-valent phosphorus derivatives **12** and **13** followed by their subsequent sulfuration.

Thus, the reaction of thiaphosphirane **4** with HF and MeOH leads to the cleavage of the C–S bond of the three-membered cycle (Scheme 5). The mechanism of this reaction probably involves the initial protonation of sulfur with the formation of the intermediate sulfonium cation and its subsequent rearrangement.

Comparison of the reactions of thiaphosphirane **4** with proton-containing reagents and hexafluoroacetone leads to an interesting conclusion. The reaction, for example, with methanol, which cannot be considered an oxidizing agent, leads to the opening of the thiaphosphirane ring and the formal oxidation of the phosphorus atom, whereas a strong electrophile like HFA only adds to the CSP cycle and the phosphorus atom remains three-valent.

Experimental Section

General: All operations were performed under nitrogen in a dry box. Solvents were dried and purified according to common procedures. The ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded with Varian Gemini 400 MHz, Bruker Avance 400 and JEOL FX-90Q spectrometers. The δ_H and δ_C chemical shifts are referenced to tetramethylsilane (TMS), the δ_P values were measured relative to 85% aqueous H_3PO_4 and the δ_F chemical shifts are reported relative to CCl_3F.

***P*-({[1-Cyano-3,3,3-trifluoro-2-(trifluoromethyl)propylidene][bis(diethylamino)]phosphoranyl}methyl)-*N*,*N*-diethylphosphonamidous Chloride (1):**[8] Phosphorus trichloride (45 mg, 0.325 mmol) was added to a solution of the bis(diethylamino)phosphane $[(CF_3)_2CHC(CN)](Et_2N)_2PCH_2P(NEt_2)_2$[6] (90 mg, 0.163 mmol) in hexane (3 mL) at –15 °C. The precipitate was filtered off and crystallized from hexane (1 mL). Light-yellow crystals (58.8 mg, 70%) were obtained; m.p. 78–80 °C. ^{1}H NMR ($CDCl_3$): δ = 1.16 (t, $^{3}J_{H,H}$ = 7.81 Hz, 6 H, NCH_2CH_3), 1.19 (t, $^{3}J_{H,H}$ = 7.3 Hz, 12 H, NCH_2CH_3), 2.82–2.95 (m, 2 H, P-CH_2-P), 3.03–3.30 (m, 12 H, NCH_2CH_3), 3.37 [m, 1 H, $CH(CF_3)_2$] ppm. $^{13}C\{H\}$ NMR ($CDCl_3$): δ = 11.8 (d, $^{1}J_{C,P}$ = 191 Hz, 1 C, P=*C*), 13.9 (br. s, 4 C, NCH_2CH_3), 14.1 (d, $^{3}J_{C,P}$ = 7 Hz, 2 C, NCH_2CH_3), 38.4 (dd, $^{1}J_{C,P}$ = 88, $^{1}J_{C–P}$ = 53 Hz, 1 C, P*C*H_2P), 39.9 (d, $^{2}J_{C,P}$ = 4 Hz, 6 C, NCH_2CH_3), 48.1 [dsept, $^{2}J_{C,F}$ = 29, $^{2}J_{C,P}$ = 15 Hz, 1 C, *C*H-$(CF_3)_2$], 124.2 (d, $^{2}J_{C,P}$ = 15 Hz, 1 C, *C*N), 124.3 (q, $^{1}J_{C,F}$ = 282 Hz, 2 C, *C*F_3) ppm. ^{19}F NMR ($CDCl_3$): δ = –66.5 (dd, $^{3}J_{H,F}$ = 7, $J_{P,F}$ = 3 Hz, 6 F, C*F*$_3$) ppm. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ = 61.8 [d, $^{2}J_{P,P}$ = 85 Hz, 1 P, $(Et_2N)_2P$], 130.5 (dsept, $^{2}J_{P,P}$ = 85, $J_{P,F}$ = 5 Hz, 1 P, *P*Cl) ppm. $C_{18}H_{33}ClF_6N_4P_2$ (516.88): calcd. C 41.83, H 6.44, N 10.84; found C 41.72, H 6.34, N 10.93.

***P*-({[1-Cyano-3,3,3-trifluoro-2-(trifluoromethyl)propylidene][bis(diethylamino)]phosphoranyl}methylene)-*N*,*N*-diethylphosphinous Amide (2):** DBU (21.6 mg, 0.135 mmol) was added at room temperature to a solution of chlorophosphane **1** (0.135 mmol) in C_6D_6 (0.7 mL) whilst stirring. After 5 min precipitated salt DBU hydrochloride was filtered. The reaction solution showed the following NMR spectroscopic data: ^{1}H NMR (C_6D_6): δ = 0.72 (t, $^{3}J_{H,H}$ = 7.03 Hz, 6 H, CH_2CH_3), 0.94 (t, $^{3}J_{H,H}$ = 7.03 Hz, 12 H, CH_2CH_3), 2.67–3.16 (m, 12 H, CH_2CH_3), 3.24 [sept, $^{3}J_{H,F}$ = 8.49 Hz, 1 H, C*H*$(CF_3)_2$], 5.67 (d, $^{2}J_{H,P}$ = 15.82 Hz, 1 H, PC*H*P) ppm. ^{19}F NMR (C_6D_6): δ = –67.2 [t, $^{3}J_{F,H}$ = 9, $J_{F,P}$ = 9 Hz, 6 F, $CH(CF_3)_2$] ppm. $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ = 62.2 [d, $^{2}J_{P,P}$ = 116 Hz, 1 P, $(Et_2N)_2P$], 299.6 (dsept, $^{2}J_{P,P}$ = 116, $J_{P,F}$ = 7 Hz, 1 P, *P*NEt_2) ppm.

2-{Bis(diethylamino)[2-(diethylamino)thiaphosphiran-3-yl]phosphoranylidene}-4,4,4-trifluoro-3-(trifluoromethyl)butanenitrile (4): A solution of sulfur (4.3 mg, 0.135 mmol) in C_6D_6 (0.3 mL) was added at room temperature to a solution of phosphaalkene **2** (ca. 0.135 mmol) in C_6D_6 (0.7 mL) whilst stirring. The reaction mixture showed the following spectroscopic data: ^{1}H NMR ($CDCl_3$): δ = 1.09 (t, $^{3}J_{H,H}$ = 6.83 Hz, 6 H, CH_2CH_3), 1.14 (t, $^{3}J_{H,H}$ = 6.83 Hz, 6 H, CH_2CH_3), 1.18 (t, $^{3}J_{H,H}$ = 6.83 Hz, 6 H, CH_2CH_3), 2.67 (dd, $^{2}J_{H,P}$ = 8.79, $^{2}J_{H,P}$ = 3.90 Hz, 1 H, PC*H*P), 2.86–3.36 (m, 12 H, CH_2CH_3), 3.39 [sept, $^{3}J_{H,F}$ = 7.81 Hz, 1 H, C*H*$(CF_3)_2$] ppm. $^{13}C\{H\}$ NMR ($CDCl_3$): δ = 12.3 (d, $^{1}J_{C,P}$ = 185 Hz, 1 C, P=*C*), 13.8 (br. s, 2 C, NCH_2CH_3), 14.1 (d, $^{3}J_{C,P}$ = 2 Hz, 2 C, NCH_2CH_3), 15.0 (d, $^{3}J_{C,P}$ = 4 Hz, 2 C, NCH_2CH_3), 22.7 (dd, $^{1}J_{C,P}$ = 108, $^{1}J_{C,P}$ = 60 Hz, 1 C, P*C*HP), 40.0 (br. s, 4 C, NCH_2CH_3), 41.4 (d, $^{2}J_{C,P}$ = 18 Hz, 2 C, NCH_2CH_3), 48.4 [m, 1 C, *C*H$(CF_3)_2$], 124.5 [q, $^{1}J_{C,F}$ = 285 Hz, 2 C, CH(*C*$F_3)_2$], 124.8 (d, $^{2}J_{C,P}$ = 12 Hz, 1 C, *C*N) ppm. ^{19}F NMR ($CDCl_3$): δ = –67.7 (quint, $^{4}J_{F,F}$ = $^{3}J_{F,H}$ = 9 Hz, 3 F, C*F*$_3$), –68.0 (m, 3 F, C*F*$_3$) ppm. $^{31}P\{H\}$ NMR ($CDCl_3$): δ = –36.5 (d, $^{2}J_{P,P}$ = 43 Hz, 1 P, *P*NEt_2), 66.3 [d, $^{2}J_{P,P}$ = 43 Hz, 1 P, $(Et_2N)_2P$] ppm. MS (APCI): *m*/*z* = 513 $[M + H]^+$.

2-{Bis(diethylamino)[2-(diethylamino)-5,5-bis(trifluoromethyl)-1,4,2-oxathiaphospholan-3-yl]phosphoranylidene}-4,4,4-trifluoro-3-(trifluoromethyl)butanenitrile (8): Hexafluoroacetone (HFA; 3 mL, 0.135 mmol) was slowly bubbled through a solution of thiaphosphirane **4** (ca. 0.1 mmol) in toluene (0.7 mL) for 5 min. The solvent was removed under reduced pressure and the residue was crystallized from hexane (1 mL). Light-yellow crystals (30 mg, ca. 44%) were obtained; m.p. 123–124 °C. ^{1}H NMR ($CDCl_3$): δ = 1.21 (t, $^{3}J_{H,H}$ = 7.07 Hz, 6 H, CH_2CH_3), 1.21 (t, $^{3}J_{H,H}$ = 7.07 Hz, 6 H, CH_2CH_3), 1.22 (t, $^{3}J_{H,H}$ = 7.07 Hz, 6 H, CH_2CH_3), 3.11 [sept, $^{3}J_{H,F}$ = 7.74 Hz, 1 H, C*H*$(CF_3)_2$], 3.15–3.33 (m, 12 H, CH_2CH_3), 4.01 (dd, $^{2}J_{H,P}$ = 6.85, $^{2}J_{H,P}$ = 1.77 Hz, 1 H, PC*H*P) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$): δ = 13.2 (d, $^{3}J_{C,P}$ = 3 Hz, 2 C, NCH_2CH_3), 13.3 (dd, $^{3}J_{C,P}$ = 3, $^{5}J_{C,P}$ = 2 Hz, 2 C, NCH_2CH_3), 14.8 (d, $^{1}J_{C,P}$ = 189 Hz, 1 C, P=*C*), 14.9 (d, $^{3}J_{C,P}$ = 4 Hz, 2 C, NCH_2CH_3), 39.8 (dd, $^{2}J_{C,P}$ = 5, $^{4}J_{C,P}$ = 4 Hz, 2 C, N*C*H_2CH_3), 40.1 (dd, $^{2}J_{C,P}$ = 8, $^{4}J_{C,P}$ = 4 Hz, 2 C, N*C*H_2CH_3), 43.5 (dd, $^{1}J_{C,P}$ = 89, $^{1}J_{C,P}$ = 70 Hz, 1 C, P*C*HP), 47.7 [m, 1 C, *C*H$(CF_3)_2$], 86.1 [m, 1 C, *C*$(CF_3)_2$], 122.0 [q, $^{1}J_{C,F}$ = 285 Hz, 2 C, CH(*C*$F_3)_2$], 123.0 (d, $^{2}J_{C,P}$ = 14 Hz, 1 C, *C*N), 124.2 (q, $^{1}J_{C,F}$ = 284 Hz, 1 C, *C*F_3), 124.4 (q, $^{1}J_{C,F}$ = 285 Hz, 1 C, *C*F_3) ppm. ^{19}F NMR ($CDCl_3$): δ = –78.4 [d, $^{3}J_{F,H}$ = 8 Hz, 6 F, $CH(CF_3)_2$], –87.5 (dq, $^{4}J_{F,P}$ = 12, $^{4}J_{F,F}$ = 10 Hz, 3 F, C*F*$_3$), –88.7 (q, $^{4}J_{F,F}$ = 10 Hz, 3 F, C*F*$_3$) ppm. $^{31}P\{H\}$ NMR ($CDCl_3$): δ = 60.7 [d, $^{2}J_{P,P}$ = 54 Hz, 1 P, $(Et_2N)_2P$], 165.7 (dq, $^{2}J_{P,P}$ = 54, $^{4}J_{P,F}$ = 12 Hz, 1 P, *P*NEt_2) ppm. MS (APCI): *m*/*z* = 679 $[M + H]^+$. $C_{21}H_{32}F_{12}N_4OP_2S$ (678.51): calcd. C 37.17, H 4.75; found C 36.97, H 4.79.

***O*-Methyl *P*-({[1-Cyano-3,3,3-trifluoro-2-(trifluoromethyl)propylidene][bis(diethylamino)]phosphoranyl}methyl)-*N*,*N*-diethylphosphonamidothioate (11):** Excess methanol (10 equiv.) was added to a solution of thiaphosphirane **4** (ca. 0.135 mmol) in toluene (0.7 mL). After 30 min solvent was removed under reduced pressure and the residue was crystallized from hexane (2 × 2 mL). Light-yellow crystals (35 mg, ca. 48%) were obtained; m.p. 107–108 C. ^{1}H NMR ($CDCl_3$): δ = 1.12 (t, $^{3}J_{H,H}$ = 6.84 Hz, 6 H, CH_2CH_3), 1.17 (t, $^{3}J_{H,H}$ = 7.81 Hz, 6 H, CH_2CH_3), 1.19 (t, $^{3}J_{H,H}$ = 7.81 Hz, 6 H, CH_2CH_3), 2.69 (q, $^{2}J_{H,H}$ = $^{2}J_{H,P1}$ = $^{2}J_{H,P2}$ = 16.60 Hz, 1 H, PC*H*P), 3.00 (dt,

$^2J_{H,P}$ = 20.51, $^2J_{P,H}$ = 15.62, $^2J_{H,H}$ = 15.62 Hz, 1 H, PC*H*P), 3.07–3.31 (m, 12 H, CH_2CH$_3$), 3.56 (d, $^3J_{H,P}$ = 14.65 Hz, 3 H, OCH_3), 3.59 [m, 1 H, C*H*(CF$_3$)$_2$] ppm. ^{13}C{H} NMR (CDCl$_3$): δ = 13.3 (br. d, $^1J_{C,P}$ = 193 Hz, 1 C, P=*C*), 14.0 (d, $^3J_{C,P}$ = 4 Hz, 2 C, NCH$_2$*C*H$_3$), 14.1 (d, $^3J_{C,P}$ = 3 Hz, 2 C, NCH$_2$*C*H$_3$), 14.5 (br. d, $^3J_{C,P}$ = 2 Hz, 2 C, NCH$_2$*C*H$_3$), 35.4 (dd, $^1J_{C,P}$ = 95, $^1J_{C,P}$ = 83 Hz, 1 C, P*C*HP), 39.9 (d, $^2J_{C,P}$ = 5 Hz, 2 C, N*C*H$_2$CH$_3$), 40.6 (d, $^2J_{C,P}$ = 4 Hz, 4 C, N*C*H$_2$CH$_3$), 47.6 [m, 1 C, *C*H(CF$_3$)$_2$], 50.4 (d, $^2J_{C,P}$ = 7 Hz, 1 C, O*C*H$_3$), 124.5 (q, $^1J_{C,F}$ = 285 Hz, 1 C, *C*F$_3$), 124.7 (q, $^1J_{C,F}$ = 285 Hz, 1 C, *C*F$_3$), 124.9 (d, $^2J_{C,P}$ = 14 Hz, 1 C, *C*N) ppm. ^{19}F NMR (CDCl$_3$): δ = –78.2 (quint, $^4J_{F,F}$ = $^3J_{F,H}$ = 9 Hz, 3 F, C*F*$_3$), –78.7 (quint, $^4J_{F,F}$ = $^3J_{F,H}$ = 9 Hz, 3 F, C*F*$_3$) ppm. ^{31}P{H} NMR (CDCl$_3$): δ = 61.6 [d, $^2J_{P,P}$ = 10 Hz, 1 P, (Et$_2$N)$_2$*P*], 78.6 (d, $^2J_{P,P}$ = 10 Hz, 1 P, *P*NEt$_2$) ppm. MS (EI): *m*/*z* = 544 [M]$^+$.

Crystal Data for 8: Data were collected with a Smart Apex II Enraf–Nonius CAD4 diffractometer. $C_{21}H_{32}F_{12}N_4OP_2S$, M = 678.51, monoclinic, a = 9.5306(15), b = 15.631(2), c = 10.5283(16) Å, β = 104.282(8)°, V = 1519.9(4) Å^3, T = 296(2) K, space group $P2_1$, Z = 2, μ(Mo-K_a) = 0.308 mm^{-1}, λ = 0.71073 Å, 12870 reflections measured, 5341 unique (R_{int} = 0.0567). Final R indices R_1 = 0.0546, $wR(F^2)$ = 0.0994 [for 2909 reflections with $I/\sigma(I) > 2.0$]. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-97 program system.[9]

CCDC-780958 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Calculations: The structures of the studied compounds were fully optimized with the ORCA program package[10] using the rapid RI-DFT (RIJCOSX-B3LYP[11–13]) approach and TZVP basis sets.[14] A three-parameter hybrid functional was used including the correlated functionals of Becke[11] and Lee, Yang and Parr (B3LYP)[12]. To check if the energies of the structures were local minima, the vibration frequencies were determined computationally for the optimized geometries, calculating the first and second derivatives numerically.

The structures with the lowest total energy were reoptimized using the GAUSSIAN 03 set of programs[15] at the DFT (B3LYP[12,13]) level of approximation and with 6-31+G** basis sets. The vibration frequencies were determined computationally calculating the first and second derivatives analytically.

The NMR shielding calculations were carried out by using the GIAO approach[16] at the RHF/6-311++G(2d,p) level of approximation with the optimized geometries. As the default within the GAUSSIAN package the mentioned basis sets are defined as the proper 6-311G Pople basis sets[17] for hydrogen and the second period atoms (C, N, O, F) and the (12s,9p) McLean–Chandler basis set[18] for phosphorus and sulfur, expanded with the appropriate polarization and diffuse Gaussian functions. The theoretical isotropic magnetic shielding magnitudes σ_{iso} for the ^{31}P and ^{13}C nuclei were then converted into the corresponding δ scales calculating the σ_{iso} values for PH$_3$ [σ_{iso}(P) = 582.2 ppm, δ_P = –240 ppm[19]] and SiMe$_4$ [σ_{iso}(C) = 194.7 ppm, δ_C = 0 ppm] at the same level of approximation.

Optimized structures are presented in the graphical mode using the VMD program.[20]

Supporting Information (see footnote on the first page of this article): Tables S1 and S2 include total energy values, zero-point vibration corrections to energy, corrected energy values, lowest vibration frequencies, relative energy values for **3a**, **3b**, **4a**, **4b**, **6**–**7**, calculated at the two different approximation levels (RIJCOSX-B3LYP/TZVP and B3LYP/6-31+G**); Cartesian coordinates are given for all optimized structures; Table S3 includes calculated (GIAO B3LYP/6-311++G(2d,p)) isotropic magnetic shielding values and corresponding chemical shift magnitudes for **3a**, **4a**, **6**, **7**.

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