Stable *N*-Phosphanyl Nitrilimines: Reactivity on the Periphery of the Nitrilimine Skeleton

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Reactions involving the λ^3-phosphorus atom of *N*-[bis(diisopropylamino)phosphanyl)]-*C*-[(bis(diisopropylamino)-thiophosphoranyl]nitrilimine (**1**) are reported. Addition of elemental sulfur or selenium to **1** leads, by a formal [1+4] cycloaddition, to 1,3,4,2λ^5-thiadiazaphosphole **3a** or 1,3,4,2λ^5-selenodiazaphosphole **3b** in 85 and 84% yield, respectively. Reactions of **1** with dimethyl acetylenedicarboxylate and tetracyanoethylene afford the corresponding [2+4] adducts 1,2,3λ^5-diazaphosphinine **6** (80% yield) and 1,2,4,3λ^5-triazaphosphinine **10** (80% yield). Phenyl azide reacts with **1** with loss of nitrogen to give 1,2,4,3λ^5-triazaphosphole **15** (74% yield), while the reaction of **1** with α-diazo ketone **17** leads with conservation of the N_2 grouping to the formation of 1,2,4,3λ^5-triazaphosphole **20** (85% yield). Addition of methyl trifluoromethanesulfonate to **1** affords *N*-[bis(diisopropylamino)methylphosphonioyl]-*C*-[bis(diisopropylamino)thiophosphoranyl]nitrilimine **22**. In contrast to **1**, the new stable nitrilimine **22** is strongly electrophilic. [2+3] cycloadditions are observed with ethyl vinyl ether, styrene, methyl acrylate and phenylacetylene to furnish the corresponding pyrazolines **23**–**25** and pyrazole **26** in good yields. Water adds to **22** by a 1,3-addition process to give hydrazine **27** (88% yield). The lithium salt **30** of [bis(diisopropylamino)thiophosphoranyl](diazo)methane reacts with [bis(pentafluorophenyl)](chloro)phosphane to afford the corresponding diazo compound **32** (50% yield) while the reaction with (chloro)(phenyl)[2,4,6-tris(trifluoromethyl)phenyl]phosphane furnishes nitrilimine **33** in 82% yield. Only 1,3-addition reactions with water or diisopropylamine leading to hydrazine **34** (65% yield) and hydrazone **35** (54% yield) are observed on treatment with this new poorly reactive nitrilimine.

The existence of nitrilimines was postulated for the first time in 1948[1]. For a long time, they have been considered as short-lived intermediates and only been detected by IR and UV spectrometry in 85-K matrix[2a–c] or by mass[2c] and real-time electron spectroscopy[2d] in the gas phase. Recently, we have shown that, provided the right substituents are chosen, these nitrilium betaines can be isolated at room temperature[3]. The development of the nitrilimine chemistry is mainly due to their ability to undergo 1,3-dipolar cycloadditions, leading to a variety of 5-membered heterocycles[4]. One of the next challenge has been to demonstrate that it is possible to carry out reactions on the periphery of the nitrilimine moiety. In other words, it has been of interest to study whether a functional group, used as a substituent in a nitrilimine, can react faster than the 1,3-dipole moiety.

We have first chosen as a model for this study *N*-[bis-(diisopropylamino)phosphanyl]-*C*-[bis(diisopropylamino)-thiophosphoranyl]nitrilimine (**1**)[3a,b], the phosphanyl substituent acting as the peripheral functional group. Two types of reactions have been studied using either reagents specific to $\sigma^3\lambda^3$-phosphorus centres or reagents which are known to react both with 1,3-dipoles and with phosphorus(III).

Sulfurization of phosphanes with elemental sulfur is a very classical reaction, and it is difficult to imagine any interaction between S_8 and the nitrilimine moiety. When **1** is treated with an excess of elemental sulfur, a clean reaction takes place at 20°C which is complete after a few minutes. After workup 1,3,4,2λ^5-thiadiazaphosphole **3a** is obtained in 85% yield. The disappearance of the nitrilimine skeleton is seen in the infrared spectrum, allowing the exclusion of the possible structural isomer **2a**. A signal at δ = 145.9 [dd, *J*(PC) = 163.8 and 65.7 Hz, C=N] in the ^{13}C-NMR spectrum and the ^{31}P-NMR spectrum [δ = +86.4, +54.3, *J*(PP) = 7.2 Hz] are consistent with the proposed structure. On silica gel, derivative **3a** undergoes a hydrolysis of the phosphorus–sulfur bond leading to **4a** (58% yield). Confirmation of these structural assignments has been obtained by the reaction of nitrilimine **1** with selenium. Indeed, the analogous 1,3,4,2λ^5-selenodiazaphosphole **3b** has been isolated in 84% yield. The observation of $^1J(P_{ring}Se)$ of 464.8 Hz and ^2J(PSe) of 61.7 Hz is in perfect agreement with the proposed structure **3b**, and the hydrolysis on silica gel leads to **4b** in 45% yield. Although adducts **3** formally result from a [4+1] cycloaddition process, it is quite likely that in fact the reaction proceeds by a two-step mechanism: an electrophilic attack of sulfur or selenium on the phosphorus lone pair, which is activated by the electron-rich nitrilimine skeleton, leading to intermediates **2**, followed by a 1,5-electrocyclization[5]. The formation of 1,3,4-thiadiazoles from unstable *N*-thiocarbonyl nitrilimines has already been reported[6] (Scheme 1).

Since electron-poor alkynes are known to undergo both [3+2] cycloadditions with nitrilimines and to react with phosphanes[7], they were suitable candidates to study

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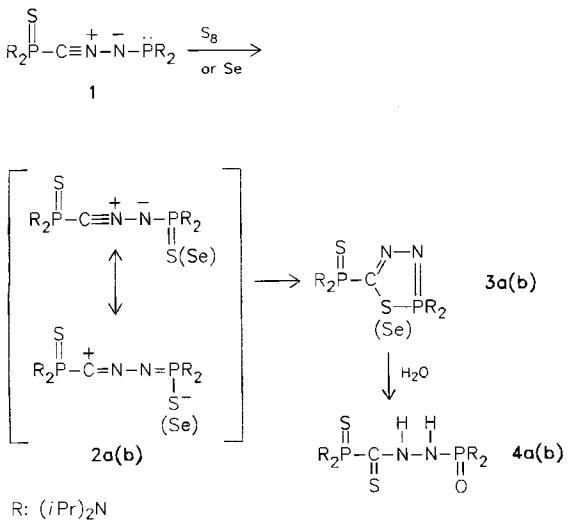
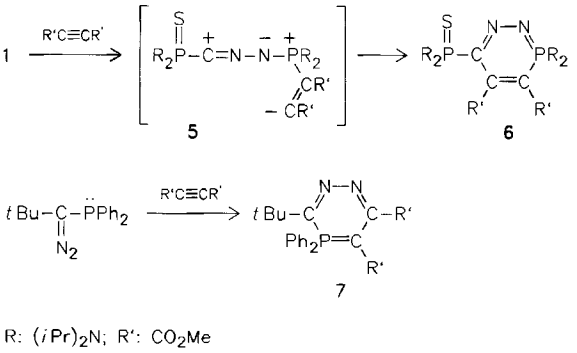
Scheme 1



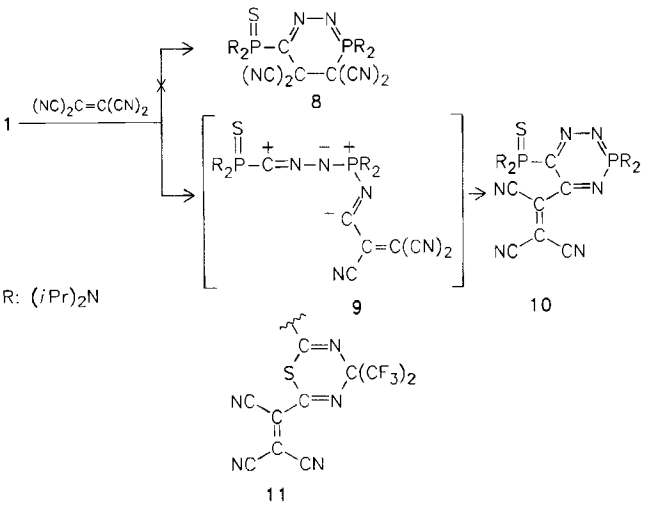
whether the phosphorus center competes with the 1,3-dipole. The reaction of **1** with a stoichiometric amount of dimethyl acetylenedicarboxylate affords the 1,2,3λ⁵-diazaphosphinine **6** as orange crystals (80% yield). Its structure has been determined by an X-ray crystal study[3e]. Although no examples of 1,6-electrocyclization involving nitrilimines are known, it is quite likely that **6** results from the electrophilic attack of the electron-poor alkyne on the phosphorus lone pair of **1**, followed by a 1,6-ring closure of intermediate **5**. This result has to be compared with the findings by Regitz et al.[8], which suggest that (diazo)(phosphanyl)alkanes formally undergo a [4+2] cycloaddition with electron-deficient alkynes to afford 1,2,4λ⁵-diazaphosphinines **7**; note that several examples of 1,3,2λ⁵-diazaphosphinines are known[9], but no derivatives of type **6** have previously been reported.

Scheme 2



It is clear that in most cases the competition between the phosphorus lone pair and the 1,3-dipole of **1** turns in favor of the dipole: even methyl acetylenecarboxylate undergoes a [2+3] cycloaddition reaction[3a,b]. However, another example of a reaction where the phosphorus lone pair reacts faster than the nitrilimine moiety is obtained by using tetracyanoethylene. The ^{31}P-NMR spectrum of the resulting product (δ = +50.67 and +22.36) demonstrates that the phosphorus atom is involved in this process. However, two adducts **8** and **10** are possible. Indeed, although addition and cycloaddition reactions of tetracyanoethylene usually proceed with high selectivity at the carbon–carbon double bond[10], a few examples of [3+2][11] and [4+2] cycloadditions[12] at one of the nitrile groups have been reported. The possible formation of **8** is readily ruled out by the presence of two signals at δ > 150 in the ^{13}C-NMR spectrum. The assignments of the ^{13}C-NMR signals of 1,2,4,3λ⁵-triazaphosphinine **10** have been accomplished by a comparison with the ^{13}C-NMR spectrum reported for **11**[12]. The attack of the phosphorus lone pair at the nitrogen of the nitrile, instead of carbon, might be explained by the structure of intermediate **9** where the negative charge can be delocalized. Note, that the only previous examples of triazaphosphinines are the 1,3,5,2λ⁵-triazaphosphinines[13] (Scheme 3).

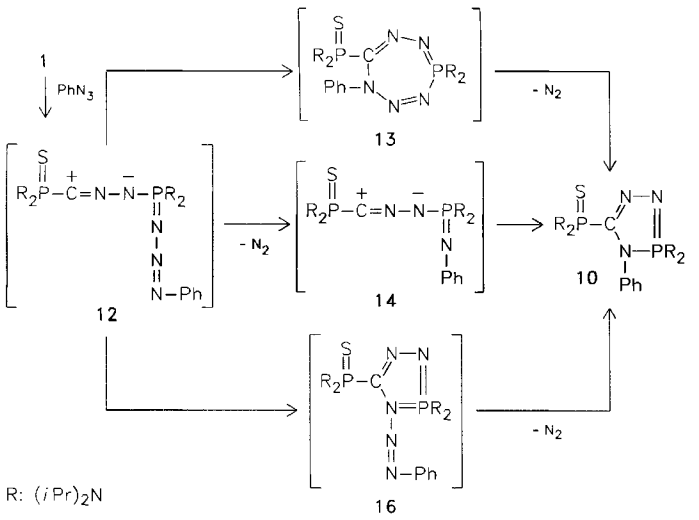
Scheme 3



Having shown that formal [4+1] and [4+2] cycloadditions can occur with **1**, we have investigated the possibility of a [4+3] cycloaddition. Azides are known to react with phosphanes to give iminophosphanes via phosphazides[14]. Thus, a 1,7-electrocyclization can be expected, leading to the seven-membered ring **13**. In fact, evolution of nitrogen is observed during the course of the reaction of phenyl azide with **1**, and the spectroscopic data are in agreement with the formation of 1,2,4,3λ⁵-triazaphosphole **15** (74% yield). This reaction probably involves the primary formation of phosphazide **12**. This compound can lose N_2 to give **14** which may undergo a 1,5-electrocyclization[15] leading to **15**. However, alternative mechanisms involving the transient formation of the desired seven-membered ring **13** or of derivative **16** can not be excluded (Scheme 4).

In order to clarify the mechanism and in the hope of obtaining a formal [4+3] adduct we have investigated the reaction of **1** with α-diazo ketone **17**, since phosphazines are known to be more stable than phosphazides[16]. According to the spectroscopic data, we have obtained the *N*-substituted 1,2,4,3λ⁵-triazaphosphole **20** (85% yield) and not the desired seven-membered ring **19**. Indeed, according to the presence of two signals at δ = 144.4 [dd, *J*(PC) = 168.0

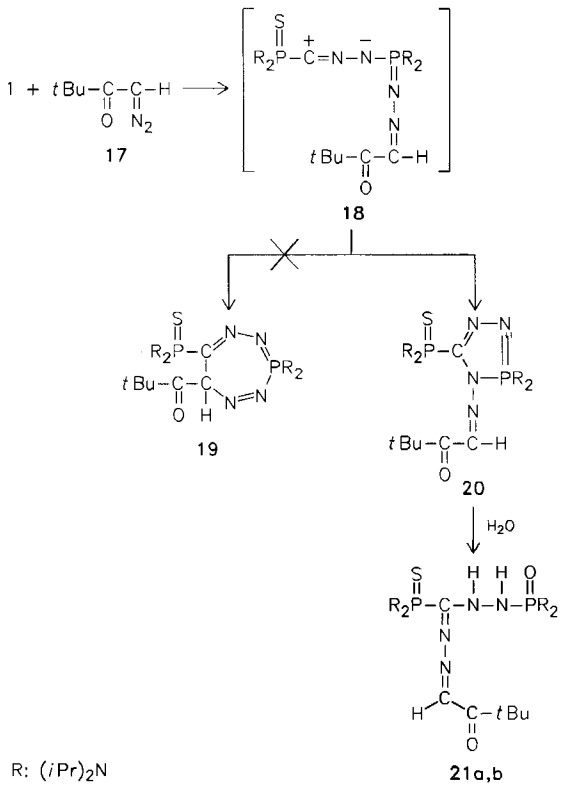
Scheme 4



R: $(i\text{Pr})_2\text{N}$

and 72.8 Hz] and 146.4 [d, *J*(PC) = 6.5 Hz, CH] in the ^{13}C-NMR spectrum the existence of structure **19** can be easily excluded. On silica gel cleavage of the phosphorus–nitrogen bond of the ring with formation of **21** (two isomers; Scheme 5) occurs.

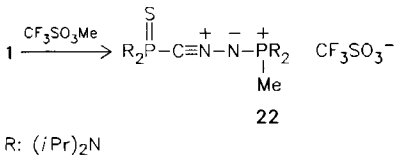
Scheme 5



R: $(i\text{Pr})_2\text{N}$

These results clearly indicate that indeed the phosphorus center is a second site of reactivity of nitrilimine **1**, but in all these reactions the nitrilimine skeleton is also involved. The next challenge has been to find a reagent which reacts at phosphorus but without subsequent reaction with the CNN fragment. It has appeared that **1** cleanly reacts with a stoichiometric amount of methyl trifluoromethanesulfonate affording a new nitrilimine **22** in 87% yield. This compound is perfectly stable at room temperature and obtained as white crystals (mp 100–102 °C) after recrystallization from a THF/ether solution. In contrast to **1**, derivative **22** is poorly soluble in nonpolar solvents, suggesting an ionic structure. The presence of the methyl group at phosphorus is revealed by the ^{1}H- [δ = 2.12, d, $J_{(PH)}$ = 13.3 Hz, 3H] and ^{13}C-NMR spectrum [δ = 16.71, d, $J_{(PC)}$ = 87.9 Hz]. The rather high-field ^{31}P-NMR chemical shift of the λ^5-phosphorus atom (δ = +28.75)[3b], the small phosphorus-phosphorus coupling constant [$^4J_{(PP)}$ = 6.7 Hz], and the ^{13}C-NMR signal of the quaternary carbon [δ = 69.83, dd, $J_{(PC)}$ = 90.3 and 17.7 Hz] are consistent with the nitrilimine structure which has been ascertained by an X-ray crystal study[3f] (Scheme 6).

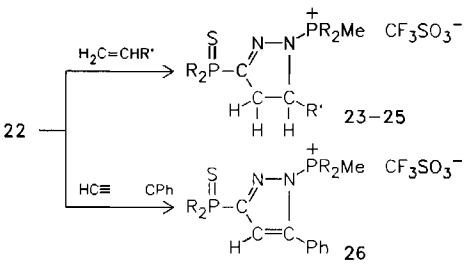
Scheme 6



R: $(i\text{Pr})_2\text{N}$

In contrast to all the known transient and stable nitrilimines, **22** is strongly electrophilic. It reacts with an electron-rich olefin such as ethyl vinyl ether at room temperature, while styrene requires 14 h at 60 °C, and 20 h at 80 °C are necessary for the electron-poor olefin methyl acrylate to react with **22**. The reaction with phenylacetylene is complete after 14 h at 60 °C. The relative dipolarophility of **1** is confirmed by competition experiments. The dipole and two dipolarophiles are mixed together in a 1:2:2 ratio in a benzene solution. The results are compared in Table 1 with the relative rates of cycloaddition of the diphenylnitrilimine with similar dipolarophiles which clearly demonstrate the strong electrophilic character of nitrilimine **22**. All these reactions occur with complete regiospecificity (according to NMR spectroscopy)[17], yielding the 5-substituted pyrazolines **23**–**25** or pyrazole **26** in good yields (Scheme 7).

Scheme 7



R: $(i\text{Pr})_2\text{N}$

	R'
23	OEt
24	Ph
25	CO_2Me

Table 1. Comparison of dipolarophilic reactivities of various carbon–carbon multiple-bond compounds with nitrilimine **22** and diphenylnitrilimine and product ratios (see Scheme 7)

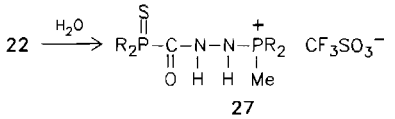
Dipolarophiles	1,3-Dipole **22** Product ratio	1,3-Dipole Diphenyl-nitrilimine[21] Product ratio
$RO_2CCH=CH_2$ [a]	15	97
$PhCH=CH_2$	85	3
$R'OCH=CH_2$ [a]	100	16
$PhCH=CH_2$	0	84
$PhC\equiv CH$	100	7
$PhCH=CH_2$	0	93

[a] R = Et, R′ = Bu in the case of diphenylnitrilimine and R = Me, R′ = Et in the case of **22**.

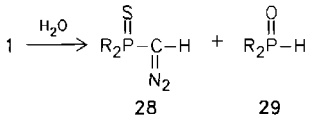
These results, as a whole, are in good agreement with calculations[18] which predict that the presence of a strong electron-withdrawing substituent decreases the HOMO and LUMO energies of the dipole, increases its electrophilicity and makes the cycloaddtion LUMO(dipole)-controlled, which favors the 5-substituted regioisomer.

Nitrilimine **22** reacts with water by a 1,3-addition process, leading to **27**. This is in marked contrast with the behavior of **1**, where the phosphorus-nitrogen bond is cleaved by water leading to the (diazo)(thiophosphoranyl)methane **28** and the phosphane oxide **29**[3b] (Scheme 8).

Scheme 8



27

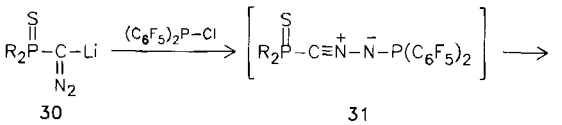


28 **29**

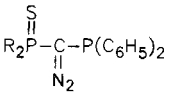
R: $(iPr)_2N$

Since nitrilimine **22** does not easily react with electron-poor dipolarophiles, it has been of interest to synthesize an *N*-phosphanylnitrilimine having an electron-withdrawing group at phosphorus, in order to decrease the reactivity of the 1,3-dipole and thus to favor the reaction at phosphorus, in the hope of enlarging the scope of the [4+*x*] cycloaddition reactions. We have first used pentafluorophenyl substituents. In fact, the lithium salt **30**[3b] of [bis(diisopropylamino)thiophosphoranyl](diazo)methane reacts with [bis(pentafluorophenyl)](chloro)phosphane[19] to give the corresponding diazo compound **32** (50% yield). Even at −78 °C, the desired nitrilimine **31** has not been observed. This result is not really surprising since we have shown that bulky substituents at phosphorus are necessary to stabilize the nitrilimine moiety[3] (Scheme 9).

Scheme 9



30 **31**

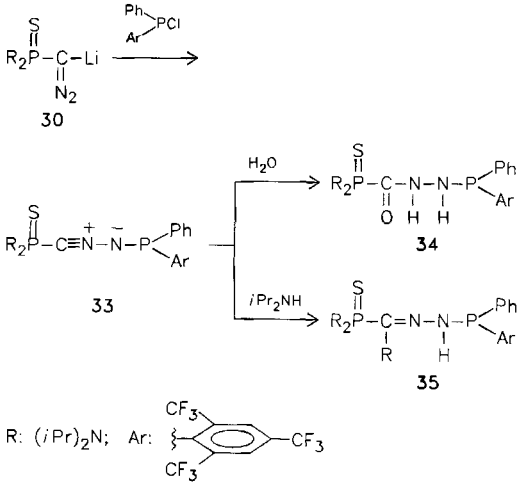


32

R: $(iPr)_2N$

In contrast, the use of (chloro)(phenyl)[2,4,6-tris(trifluoromethyl)phenyl]phosphane[20] has allowed us to obtain nitrilimine **33** (82% yield) which appears to be stable for several months at room temperature. As desired, nitrilimine **33** does not undergo [3+2] cycloaddition reactions with electron-poor dipolarophiles such as methyl acrylate or dimethyl maleate, but surprisingly it does not react either with electron-rich dipolarophiles (ethyl vinyl ether). It is thus clear that the nitrilimine skeleton of **33** is desactivated to give a high probability for reactions at the λ^3-phosphorus atom. Unfortunately, no reaction occurs with dimethyl acetylenedicarboxylate or tetracyanoethylene indicating the very low reactivity of the λ^3-phosphorus atom. This might be due to electronic factors but also to the excessive steric hindrance induced by the 2,4,6-tris(trifluromethyl)phenyl substituent. In fact, **33** is so unreactive that it can be isolated by column chromatography on silica gel. The only reactions observed are very slow and involve 1,3-addition processes with water or diisopropylamine leading to adducts **34** and **35**, respectively (Scheme 10).

Scheme 10



30 **33** **34** **35**

R: $(iPr)_2N$; Ar:

It is clear from these results that it is possible to carry out reactions on the periphery of the nitrilimine skeleton which enlarges enormously the scope of application of these dipoles.

Experimental

All experiments were carried out under dry nitrogen. All solvents were freshly distilled from appropriate drying agents. – IR: Perkin-Elmer 597. – ^{1}H, ^{13}C and ^{29}Si NMR: Bruker AC 200 and AM 300. ^{31}P NMR: Bruker AC 80; ^{1}H-, ^{13}C- and ^{29}Si-NMR chemical shifts (δ) are reported relative to Me_4Si as external standard; ^{31}P-NMR downfield shifts are expressed with a positive sign, relative to external 85% H_3PO_4. – MS: Ribermag R 10 10E. – Melting points: Electrothermal 1A. – TLC: chromagel 60 A CC; ether and hexane as eluents.

Preparation of the Adducts and Cycloadducts of **1** *(General Procedure):* Equimolar quantities of **1**[3c] and the desired reagent in 10–20 ml of the appropriate solvent were mixed at −78°C or room temperature. After 1 or 2 h, the solvent was evaporated, the residue washed and directly analysed or first recrystallized. Amounts of starting materials, solvent and temperature are given for each compound.

1,3,4,2λ⁵-Thiadiazaphosphole **3a**: Sulfur: 0.02 g (0.56 mmol); **1**: 0.30 g (0.56 mmol); pentane; room temperature. After stirring for 2 h and filtration, the solvent was removed and the residue washed with cold pentane to give **3a** as a yellow oil; yield 0.27 g (85%). – ^{31}P NMR ($CDCl_3$): δ = 86.4, 54.3 [^4J(PP) = 7.2 Hz]. – ^{1}H NMR ($CDCl_3$): δ = 1.30 [d, ^3J(HH) = 7.0 Hz, 12H, $(CH_3)_2CH$)], 1.40 [d, ^3J(HH) = 7.0 Hz, 12H, $(CH_3)_2CH$], 1.60 [d, ^3J(HH) = 7.0 Hz, 12H, $(CH_3)_2CH$], 1.70 [^3J(HH) = 7.0 Hz, 12H, $(CH_3)_2CH$], 3.60 [septd, ^3J(HH) = 7.0 Hz, ^3J(PH) = 18.0 Hz, 4H, $(CH_3)_2CH$], 4.20 [septd, ^3J(HH) = 7.0 Hz, ^{3}J(PH) = 17.0 Hz, 4H, $(CH_3)_2CH$]. – ^{13}C NMR ($CDCl_3$): δ = 22.64, 22.67, 23.17, 23.20, 23.82, 23.86, 23.90, 23.94 [s, $(CH_3)_2CH$], 47.69 [d, ^2J(PC) = 5.5 Hz, $(CH_3)_2CH$], 48.11 [d, ^2J(PC) = 3.5 Hz, $(CH_3)_2CH$], 145.90 [dd, J(PC) = 163.8 and 65.7 Hz, C=N]. – MS (70 eV): m/z = 566 [M^+].

Hydrazine **4a**: Attempted purification of **3a**, obtained as previously mentioned, on silica gel using ether as eluent afforded **4a** as a colorless oil; yield 0.19 g (58%). – R_f = 0.8 (ether). – ^{31}P NMR ($CDCl_3$): δ = 62.75, 14.84 [^4J(PP) = 1.5 Hz]. – ^{1}H NMR ($CDCl_3$): δ = 1.18 [d, ^3J(HH) = 6.8 Hz, 12H, $(CH_3)_2CH$], 1.21 [d, ^3J(HH) = 6.8 Hz, 12H, $(CH_3)_2CH$], 1.27 [d, ^3J(HH) = 6.9 Hz, 12H, $(CH_3)_2CH$], 1.31 [d, ^3J(HH) = 6.9 Hz, 12H, $(CH_3)_2CH$], 3.47 [septd, ^3J(HH) = 6.8 Hz, ^3J(PH) = 17.9 Hz, 4H, $(CH_3)_2CH$], 3.89 [septd, ^3J(HH) = 6.9 Hz, ^3J(PH) = 16.1 Hz, 4H, $(CH_3)_2CH$], 8.18 (t-like, 2H, NH). – ^{13}C NMR ($CDCl_3$): δ = 22.46, 23.30, 23.71, 23.83 [s, $(CH_3)_2CH$], 46.50 [d, ^2J(PC) = 5.0 Hz, $(CH_3)_2CH$], 48.00 [d, ^2J(PC) = 5.0 Hz, $(CH_3)_2CH$], 175.85 [dd, J(PC) = 111.6 and 5.6 Hz, C=S]. – MS (70 eV): m/z = 584 [M^+].

$C_{25}H_{58}N_6OP_2S_2$ (584.85) Calcd. C 51.34 H 10.00 N 14.38
Found C 51.20 H 9.84 N 14.45

1,3,4,2λ⁵-Selenodiazaphosphole **3b**: Selenium: 0.05 g (0.56 mmol); **1**: 0.30 g (0.56 mmol); pentane; room temperature. After stirring for 2 h, the solvent was removed and the product **3b** obtained as colorless crystals from cold pentane; yield 0.29 g (84%), mp 160°C. – ^{31}P NMR ($CDCl_3$): δ = 91.60, 55.70 [^4J(PP) < 1 Hz, J(PSe) = 464.8 and 61.7 Hz]. – ^{1}H NMR ($CDCl_3$): δ = 1.14 [d, ^3J(HH) = 6.9 Hz, 12H, $(CH_3)_2CH$], 1.19 [d, ^3J(HH) = 6.9 Hz, 12H, $(CH_3)_2CH$], 1.23 [d, ^3J(HH) = 6.9 Hz, 12H, $(CH_3)_2CH$], 1.27 [d, ^3J(HH) = 6.9 Hz, 12H, $(CH_3)_2CH$], 3.67 [septd, ^3J(HH) = 6.9 Hz, ^3J(PH) = 18.1 Hz, 4H, $(CH_3)_2CH$], 3.86 [septd, ^3J(HH) = 6.9 Hz, ^3J(PH) = 17.0 Hz, 4H, $(CH_3)_2CH$]. – ^{13}C NMR ($CDCl_3$): δ = 22.21, 22.24, 23.37, 23.41, 23.45, 23.48, 23.49, 23.53 [s, $(CH_3)_2CH$], 47.19 [d, ^2J(PC) = 6.0 Hz, $(CH_3)_2CH$], 48.06 [d, ^2J(PC) = 3.8 Hz, $(CH_3)_2CH$], 149.00 [dd, J(PC) = 154.7 and 70.2 Hz, C=N]. – MS (70 eV): m/z = 613 [M^+].

$C_{25}H_{56}N_6P_2SSe$ (613.73) Calcd. C 48.84 H 9.19 N 13.68
Found C 48.92 H 9.03 N 13.76

Hydrazine **4b**: On silica gel and with ether as eluent **3b** was hydrolyzed to afford **4b** as a colorless oil; yield 0.16 g (45%). – R_f = 0.8 (ether). – ^{31}P NMR ($CDCl_3$): δ = 64.80, 13.70 [^4J(PP) < 1.0 Hz]. – ^{1}H NMR ($CDCl_3$): δ = 1.15 [d, ^3J(HH) = 7.0 Hz, 24H, $(CH_3)_2CH$], 1.34 [d, ^3J(HH) = 7.0 Hz, 12H, $(CH_3)_2CH$], 1.35 [d, ^3J(HH) = 7.0 Hz, 12H, $(CH_3)_2CH$], 3.60 [m$_c$, 8H, $(CH_3)_2CH$]. – ^{13}C NMR ($CDCl_3$): δ = 23.20, 23.39, 23.90, 23.92 [s, $(CH_3)_2CH$], 46.47 [d, ^2J(PC) = 4.9 Hz, $(CH_3)_2CH$], 47.97 [s, $(CH_3)_2CH$], 173.75 [d, ^1J(PC) = 95.09 Hz, C=Se). – MS (70 eV): m/z = 631 [M^+].

$C_{25}H_{58}N_6OP_2SSe$ (631.75) Calcd. C 47.45 H 9.24 N 13.29
Found C 47.31 H 9.02 N 13.42

1,2,3,λ⁵-Diazaphosphinine **6**: Dimethyl acetylenedicarboxylate: 0.08 g (0.56 mmol); **1**: 0.30 g (0.56 mmol); benzene; room temperature. After filtration and evaporation of the solvent, the residue was recrystallized from cold pentane. Compound **6** was obtained as orange crystals; yield 0.30 g (80%), mp 147°C – IR (KBr): $\tilde{\nu}$ = 1705 and 1740 cm^{-1} (C=O). – ^{31}P NMR ($CDCl_3$): δ = 68.60, 14.50 [^4J(PP) = 4.4 Hz]. – ^{1}H NMR ($CDCl_3$): δ = 1.05 [d, ^3J(HH) = 7.0 Hz, 12H, $(CH_3)_2CH$], 1.30 [d, ^3J(HH) = 7.0 Hz, 12H, $(CH_3)_2CH$], 1.55 [d, ^3J(HH) = 7.0 Hz, 24H, $(CH_3)_2CH$], 3.30 (s, 3H, CH_3O), 3.75 (s, 3H, CH_3O), 4.20 [m$_c$, 8H, $(CH_3)_2CH$]. – ^{13}C NMR ($CDCl_3$): δ = 23.34, 24.07, 24.42, 25.01 [s, $(CH_3)_2CH$], 47.07 [d, ^2J(PC) = 5.3 Hz, $(CH_3)CH$], 47.62 [d, ^2J(PC) = 6.0 Hz, $(CH_3)_2CH$], 52.37 and 52.44 (s, CH_3O), 92.19 [dd, J(PC) = 107.5 and 11.7 Hz, PCCO], 138.74 [d, ^2J(PC) = 31.7 Hz, CCP], 141.59 [dd, J(PC) = 171.7 and 54.7 Hz, C=N], 166.57 (s, C=O).

$C_{31}H_{62}N_6O_4P_2S$ (676.88) Calcd. C 55.00 H 9.24 N 12.42
Found C 54.72 H 9.27 N 12.46

1,2,4,3λ⁵-Triazaphosphinine **10**: Tetracyanoethylene: 0.07 g (0.56 mmol); **1**: 0.30 g (0.56 mmol); THF; −78°C. After warming up and evaporation of the solvent, the residue was washed several times with cold pentane. Cycloadduct **10** was obtained as a brown oil; yield 0.30 g (80%). ^{31}P NMR ($CDCl_3$): δ = 50.67, 22.36 [^4J(PP) < 1.0 Hz]. – ^{1}H NMR ($CDCl_3$): δ = 1.15 [d, ^3J(HH) = 7.0 Hz, 12H, $(CH_3)_2CH$], 1.20 [d, ^3J(HH) = 6.8 Hz, 12H, $(CH_3)_2CH$], 1.22 [d, ^3J(HH) = 6.8 Hz, 12H, $(CH_3)_2CH$], 1.38 [d, ^3J(HH) = 7.0 Hz, 12H, $(CH_3)_2CH$], 3.91 [septd, ^3J(HH) = 7.0 Hz, ^3J(PH) = 17.2 Hz, 4H, $(CH_3)_2CH$], 3.93 [septd, ^3J(HH) = 6.8 Hz, ^3J(PH) = 20.2 Hz, 4H, $(CH_3)_2CH$]. – ^{13}C NMR ($CDCl_3$):δ = 21.28, 21.31, 22.48, 22.51, 23.37, 23.39, 23.41, 23.42 [s, $(CH_3)_2CH$], 47.26 [d, ^2J(PC) = 6.0 Hz, $(CH_3)_2CH$], 48.92 [d, ^2J(PC) = 4.5 Hz, $(CH_3)_2CH$], 89.95 [d, ^4J(PC) = 8.3 Hz, $C(CN)_2$], 106.75 (s, CN), 107.04 [d, ^4J(PC) = 1.5 Hz, CN], 108.14 (s, CN), 149.16 [d, ^3J(PC) = 4.5 Hz, CCN], 153.20 [dd, ^2J(PC) = 10.6 and 8.3 Hz, CC=N], 168.00 [dd, J(PC) = 158.1 and 14.0 Hz, PC=N].

$C_{31}H_{56}N_{10}P_2S$ (662.87) Calcd. C 56.16 H 8.52 N 21.14
Found C 56.24 H 8.45 N 21.30

1,2,4,3λ⁵-Triazaphosphole **15**: Phenyl azide: 0.07 g (0.56 mmol); **1**: 0.30 g (0.56 mmol); THF; −78°C. After warming up and evaporation of the solvent, the residue was washed several times with cold pentane to afford **15** as a yellow oil; yield 0.27 g (74%). – ^{31}P NMR ($CDCl_3$): δ = 57.30, 37.90 [^4J(PP) = 8.2 Hz]. – ^{1}H NMR ($CDCl_3$): δ = 1.13 [d, ^3J(HH) = 6.8 Hz, 12H, $(CH_3)_2CH$], 1.17 [d, ^3J(HH) = 6.8 Hz, 12H, $(CH_3)_2CH$], 1.35 [d, ^3J(HH) = 6.9 Hz, 24H, $(CH_3)_2CH$], 3.52 [septd, ^3J(HH) = 6.8 Hz, ^3J(PH) = 18.4 Hz, 4H, $(CH_3)_2CH$], 3.85 [septd, ^3J(HH) = 6.9 Hz, ^3J(PH) = 16.5 Hz, 4H, $(CH_3)_2CH$]. – ^{13}C NMR ($CDCl_3$): δ = 22.88, 22.90, 23.14, 23.17,

23.85, 23.89, 24.21 [s, $(CH_3)_2CH$], 48.28 [d, $^2J(PC)$ = 6.3 Hz, $(CH_3)_2CH$], 48.47 [d, $^2J(PC)$ = 4.3 Hz, $(CH_3)_2CH$], 122.66 (s, C-*o*), 128.81 (s, C-*p*), 128.97 (s, C-*m*), 145.14 [dd, $J(PC)$ = 171.1 and 66.7 Hz, C=N], 148.55 (s, C-*i*).

$C_{31}H_{61}N_7P_2S$ (625.87) Calcd. C 59.48 H 9.83 N 15.67
Found C 59.30 H 9.90 N 15.53

1,2,4,3λ⁵-Triazaphosphole **20**: **17**: 0.07 g (0.56 mmol); **1**: 0.30 g (0.56 mmol); THF; −78°C. After warming up and evaporation of the solvent, the residue was washed several times with cold pentane to give **20** as a yellow oil; yield 0.31 g (85%). − ^{31}P NMR (THF): δ = 61.10, 48.50 [$^4J(PP)$ = 10.7 Hz]. − ^{1}H NMR ($CDCl_3$): δ = 1.26 (m_c, 57H, CH_3), 3.76 [m_c, 8H, $(CH_3)_2CH$], 8.72 (s, 1H, NCH). − ^{13}C NMR ($CDCl_3$): δ = 22.65, 23.15, 23.50, 23.54, 24.15 (s, $(CH_3)_2CH$], 26.20 [s, $(CH_3)_3C$], 43.51 [s, $(CH_3)_3C$], 47.97 [d, $^2J(PC)$ = 8.2 Hz, $(CH_3)_2CH$], 48.11 [d, $^2J(PC)$ = 5.6 Hz, $(CH_3)_2CH$], 144.46 [dd, $J(PC)$ = 168.0 and 72.8 Hz, C=N], 146.39 [d, $^3J(PC)$ = 6.5 Hz, HCN], 203.71 (s, C=O). − MS (70 eV): *m/z* = 661 [M^+].

Hydrazine **21**: Attempted purification of **20** on silica gel gave a mixture of two isomers (**a**/**b** = 75:25) as a yellow oil; yield 0.25 g (80%). − R_f = 0.4 [hexane/ether (50:50)]. − ^{31}P NMR ($CDCl_3$): δ(**a**) = 59.59, 11.28 [$^4J(PP)$ = 2.2 Hz]; δ(**b**) = 59.07, 12.84 [$^4J(PP)$ = 2.1 Hz). − ^{1}H NMR ($CDCl_3$): δ = 1.19 [d, $^3J(HH)$ = 6.7 Hz, 12H, $(CH_3)_2CH$(**a**)], 1.20 [s, 9H, $(CH_3)_3C$(**a**)], 1.26 [d, $^3J(HH)$ = 6.7 Hz, 12H, $(CH_3)_2CH$(**a**)], 1.33 [d, $^3J(HH)$ = 6.8 Hz, 12H, $(CH_3)_2CH$(**a**)], 1.35 [d, $^3J(HH)$ = 6.8 Hz, 12H, $(CH_3)_2CH$(**a**)], 3.49 [septd, $^3J(HH)$ = 6.7 Hz, $^3J(PH)$ = 17.4 Hz, 4H, $(CH_3)_2CH$(**a**)], 3.86 [septd, $^3J(HH)$ = 6.8 Hz, $^3J(PH)$ = 17.4 Hz, 4H, $(CH_3)_2CH$(**a**)], 6.98 [d, $^5J(PH)$ = 1.5 Hz, 1H, HC=N(**a**)], 7.53 [d, $^5J(PH)$ = 1.2 Hz, 1H, HC=N(**b**)], 9.93 [d, $^2J(PH)$ = 24.9 Hz, 1H, PNH(**b**)], 10.24 [d, $^2J(PH)$ = 24.9 Hz, 1H, PNH(**a**)], 10.64 [s, 1H, NNH(**b**)], 14.18 [s, 1H, NNH(**a**)], the CH_3 and CH signals of the isomer **b** are obscured by those of isomer **a**. − ^{13}C NMR ($CDCl_3$): δ = 22.39, 22.86, 23.07, 23.27, 23.48, 23.63, 23.68 [s, $(CH_3)_2CH$], 26.00 [s, $(CH_3)_3C$(**b**)], 26.20 [s, $(CH_3)_3C$(**a**)], 42.81 [s, $(CH_3)_3C$(**b**)], 42.89 [s, $(CH_3)_3C$(**a**)], 45.83 [d, $^2J(PC)$ = 5.0 Hz, $(CH_3)_2CH$(**b**)], 46.10 [d, $^2J(PC)$ = 5.2 Hz, $(CH_3)_2CH$(**a**)], 47.51 [d, $^2J(PC)$ = 5.2 Hz, $(CH_3)_2CH$(**a**)], 121.72 [s, HC=N(**a**)], 130.97 [s, HC=N(**b**)], 131.74 [dd, $J(PC)$ = 176.7 and 13.8 Hz, PC=N(**b**)], 133.37 [dd, $J(PC)$ = 179.0 and 13.0 Hz, PC=N(**a**)], 198.30 [s, C=O(**b**)], 201.67 [s, C=O(**a**)]. − MS (70 eV): *m/z* = 678 [M^+].

$C_{31}H_{68}N_8O_2P_2S$ (678.95) Calcd. C 54.83 H 10.10 N 16.51
Found C 54.90 H 10.01 N 16.38

N-[Bis(diisopropylamino)methylphosphonioyl]-C-[bis(diisopropylamino)thiophosphoranyl]nitrilimine **22**: Methyl trifluoromethanesulfonate: 0.09 g (0.56 mmol); **1**: 0.30 g (0.56 mmol); pentane, room temperature. After stirring for 1 hour, the solvent was removed and the residue recrystallized from THF/ether. Nitrilimine **22** was obtained as colorless crystals; yield 0.34 g (87%), mp 100−102°C. − IR ($CDCl_3$): $\tilde{\nu}$ = 2170 cm^{-1} (CNN). − ^{31}P NMR ($CDCl_3$): δ = 52.68, 28.75 [$^4J(PP)$ = 6.7 Hz]. − ^{1}H NMR ($CDCl_3$): δ = 1.29 [d, $^3J(HH)$ = 6.9 Hz, 12H, $(CH_3)_2CH$], 1.31 [d, $^3J(HH)$ = 6.9 Hz, 12H, $(CH_3)_2CH$], 1.32 [d, $^3J(HH)$ = 6.9 Hz, 12H, $(CH_3)_2CH$], 1.33 [d, $^3J(HH)$ = 6.9 Hz, 12H, $(CH_3)_2CH$], 2.12 [d, $^2J(PH)$ = 13.3 Hz, 3H, CH_3P], 3.70 [septd, $^3J(HH)$ = 6.9 Hz, $^3J(PH)$ = 19.6 Hz, 4H, $(CH_3)_2CH$], 3.72 [septd, $^3J(HH)$ = 6.9 Hz, $^3J(PH)$ = 20.8 Hz, 4H, $(CH_3)_2CH$]. − ^{13}C NMR ($CDCl_3$): δ = 16.71 [d, $^1J(PC)$ = 87.9 Hz, CH_3P], 22.28, 22.55, 22.94, 23.20 [s, $(CH_3)_2CH$], 47.41 [d, $^2J(PC)$ = 4.9 Hz, $(CH_3)_2CH$], 47.53 [d, $^2J(PC)$ = 4.8 Hz, $(CH_3)_2CH$], 69.83 [dd, $J(PC)$ = 90.3 and 17.7 Hz, C=N], 120.91 [q, $^1J(FC)$ = 320.8 Hz, CF_3].

$C_{27}H_{59}F_3N_6O_3P_2S_2$ (698.87) Calcd. C 46.39 H 8.51 N 12.03
Found C 46.20 H 8.46 N 12.09

Cycloadducts of Nitrilimine **22** *(General Procedure)*: A stoichiometric amount of the dipolarophile was added to the nitrilimine **22** (1 mmol) in 10 ml of pentane at room temperature. After heating as indicated, the solvent was removed, and the adducts were washed with a THF/ether solution.

Pyrazoline **23**: Ethyl vinyl ether: 0.07 g (1 mmol); **1**: 0.53 g (1 mmol); 12 h at room temperature; yield 0.51 g (85%). − ^{31}P NMR ($CDCl_3$): δ = 55.77, 47.60 [$^4J(PP)$ = 1.7 Hz]. − ^{1}H NMR ($CDCl_3$): δ = 1.12 [t, $^3J(HH)$ = 7.0 Hz, 3H, CH_3CH_2], 1.27 [d, $^3J(HH)$ = 6.8 Hz, 6H, $(CH_3)_2CH$], 1.30 [d, $^3J(HH)$ = 6.8 Hz, 12H, $(CH_3)_2CH$], 1.33 [d, $^3J(HH)$ = 7.0 Hz, 24H, $(CH_3)_2CH$], 1.36 [d, $^3J(HH)$ = 6.8 Hz, 6H, $(CH_3)_2CH$], 2.30 [d, $^2J(PH)$ = 14.4 Hz, 3H, CH_3P], 3.30 [m_c, 2H, CH_2 (ring)], 3.51 (m_c, 2H, CH_3CH_2], 3.69 [septd, $^3J(HH)$ = 6.8 Hz, $^3J(PH)$ = 18.0 Hz, 2H, $(CH_3)_2CH$], 3.75 [septd, $^3J(HH)$ = 7.0 Hz, $^3J(PH)$ = 16.8 Hz, 4H, $(CH_3)_2CH$], 3.86 [septd, $^3J(HH)$ = 6.8 Hz, $^3J(PH)$ = 18.0 Hz, 2H, $(CH_3)_2CH$], 5.64 [dd, $J(HH)$ = 4.6 and 2.8 Hz, 1H, CH (ring)]. − ^{13}C NMR ($CDCl_3$): δ = 14.98 (s, CH_3CH_2), 15.08 [d, $^1J(PC)$ = 100.4 Hz, CH_3P], 23.02, 23.05, 23.38, 23.39, 23.41, 23.42, 23.46, 23.49, 23.83, 23.87, 23.99, 24.10, 24.15, 24.30, 24.35, 24.40 [s, $(CH_3)_2CH$], 43.93 [dd, $J(PC)$ = 18.7 and 6.1 Hz, CH_2 (ring)], 47.73 [d, $^2J(PC)$ = 6.0 Hz, $(CH_3)_2CH$], 48.00 [d, $^2J(PC)$ = 5.3 Hz, $(CH_3)_2CH$], 48.58 [d, $^2J(PC)$ = 5.1 Hz, $(CH_3)_2CH$], 48.65 [d, $^2J(PC)$ = 5.7 Hz, $(CH_3)_2CH$], 62.02 (s, CH_3CH_2), 88.85 [m_c, CH (ring)], 120.74 [q, $^1J(FC)$ = 320.7 Hz, CF_3], 160.08 [dd, $J(PC)$ = 140.0 and 11.2 Hz, C=N].

$C_{31}H_{67}F_3N_6O_4P_2S_2$ (770.98)
Calcd. C 48.29 H 8.76 N 10.91
Found C 48.32 H 8.56 N 10.82

Pyrazoline **24**: Styrene: 0.10 g (1 mmol); **22**: 0.53 g (1 mmol); 14 h at 60°C; yield 0.53 g (84%). − ^{31}P NMR ($CDCl_3$): δ = 49.73, 57.43 [$^4J(PP)$ = 2.4 Hz]. − ^{1}H NMR ($CDCl_3$): δ = 1.25 [d, $^3J(HH)$ = 6.7 Hz, 6H, $(CH_3)_2CH$], 1.28 [d, $^3J(HH)$ = 6.7 Hz, 6H, $(CH_3)_2CH$], 1.30 [d, $^3J(HH)$ = 6.7 Hz, 6H, $(CH_3)_2CH$], 1.33 [d, $^3J(HH)$ = 6.7 Hz, 6H, $(CH_3)_2CH$], 1.34 [d, $^3J(HH)$ = 6.9 Hz, 12H, $(CH_3)_2CH$], 2.01 [d, $^2J(PH)$ = 14.0 Hz, 3H, CH_3P], 3.33 [dd, $J(HH)$ = 18.3 and 4.3 Hz, 1H, CH_2 (ring)], 3.70 [septd, $^3J(HH)$ = 6.7 Hz, $^3J(PH)$ = 15.6 Hz, 2H, $(CH_3)_2CH$], 3.78 [septd, $^3J(HH)$ = 6.7 Hz, $^3J(PH)$ = 15.6 Hz, 2H, $(CH_3)_2CH$], 3.82 [septd, $^3J(HH)$ = 6.9 Hz, $^3J(PH)$ = 16.2 Hz, 4H, $(CH_3)_2CH$], 3.89 [dd, $^3J(HH)$ = 18.3 and 11.9 Hz, 1H, CH_2 (ring)], 5.47 [ddd, $J(HH)$ = 11.9 and 4.4 Hz, $^3J(PH)$ = 2.9 Hz, 1H, CH (ring)], 7.32 [m_c, 5H, H (arom)]. − ^{13}C NMR ($CDCl_3$): δ = 15.21 [d, $^1J(PC)$ = 102.2 Hz, CH_3P], 23.54, 23.57, 23.84, 23.88, 24.04, 24.08, 24.27, 24.28, 24.31, 24.32, 24.36, 24.39, 24.40, 24.42, 24.69, 24.73 [s, $(CH_3)_2CH$], 48.43 [d, $^2J(PC)$ = 5.5 Hz, $(CH_3)_2CH$], 48.68 [d, $^2J(PC)$ = 5.6 Hz, $(CH_3)_2CH$], 49.04 [d, $^2J(PC)$ = 5.1 Hz, $(CH_3)_2CH$], 49.10 [d, $^2J(PC)$ = 4.9 Hz, $(CH_3)_2CH$], 63.97 [dd, $J(PC)$ = 7.0 and 2.9 Hz, CH (ring)], 120.94 [q, $^1J(FC)$ = 320.2 Hz, CF_3], 126.80 (s, C-*o*), 129.28, (s, C-*p*), 129.74 (s, C-*m*), 141.46 (s, C-*i*), 160.55 [dd, $J(PC)$ = 139.3 and 11.2 Hz, C=N].

$C_{35}H_{67}F_3N_6O_3P_2S_2$ (803.03)
Calcd. C 52.34 H 8.42 N 10.47
Found C 52.12 H 8.45 N 10.32

Pyrazoline **25**: Methyl acrylate: 0.09 g (1 mmol); **22**: 0.53 g (1 mmol); 20 h at 80°C; yield 0.47 g (77%). − ^{31}P NMR ($CDCl_3$): 49.91, 56.91 [$^4J(PP)$ = 2.0 Hz]. − ^{1}H NMR ($CDCl_3$): δ = 1.33 [m_c, 48H, $(CH_3)_2CH$], 2.23 [d, $^2J(PH)$ = 14.1 Hz, CH_3P], 3.71 [m_c, 8H, $(CH_3)_2CH$], 3.75 (s, CH_3O), 5.11 [ddd, $J(HH)$ = 12.8 and 3.6 Hz, $^3J(PH)$ = 2.2 Hz, CH (ring); the signals of CH_2 (ring) are obscured by the multiplet at δ = 3.71. − ^{13}C NMR ($CDCl_3$): δ = 14.37 [d, $^1J(PC)$ = 101.9 Hz, CH_3P], 22.87, 22.89, 23.60, 23.66, 23.69, 23.73, 24.00, 24.07, [s, $(CH_3)_2CH$], 43.54 [dd, $J(PC)$ = 21.0 and 3.1 Hz, CH_2 (ring)], 48.46 [d, $^2J(PC)$ = 5.5 Hz, $(CH_3)_2CH$], 48.90 [d,

^2J(PC) = 5.7 Hz, $(CH_3)_2CH$], 53.22 (s, CH_3O), 59.61 [dd, J(PC) = 8.1 and 3.5 Hz, CH (ring)], 120.33 [q, ^1J(FC) = 319.7 Hz, CF_3], 159.48 [dd, J(PC) = 136.7 and 10.4 Hz, C=N], 171.20 (s, C=O).

$C_{31}H_{65}F_3N_6O_5P_2S_2$ (784.96)
Calcd. C 47.43 H 8.35 N 10.71
Found D 47.32 H 8.41 N 10.75

Pyrazoline **26**: Phenylacetylene: 0.10 g (1.00 mmol); **22**: 0.53 g (1 mmol); 14 h at 60°C; yield 0.66 g (82%). – ^{31}P NMR ($CDCl_3$): δ = 49.52, 56.53 [^4J(PP) = 1.6 Hz]. – ^{1}H NMR ($CDCl_3$): δ = 1.24 (d, ^3J(HH) = 6.9 Hz, 12H, $(CH_3)_2CH$], 1.28 [d, ^3J(HH) = 6.9 Hz, 12H, $(CH_3)_2CH$], 1.38 [d, ^3J(HH) = 6.9 Hz, 12H, $(CH_3)_2CH$], 1.39 [d, ^3J(HH) = 6.9 Hz, 12H, $(CH_3)_2CH$], 1.93 [d, ^2J(PH) = 14.2 Hz, 3H, CH_3P], 3.80 [septd, ^3J(HH) = 6.9 Hz, ^3J(PH) = 16.3 Hz, 4H, $(CH_3)_2CH$], 3.81 [septd, ^3J(HH) = 6.9 Hz, ^3J(PH) = 17.2 Hz, 4H, $(CH_3)_2CH$], 6.72 [d, ^3J(PH) = 2.5 Hz, 1H, CH (ring)], 7.31 [m$_c$, 3H, H (arom)], 7.56 [m$_c$, 2H, H (arom)]. – ^{13}C NMR ($CDCl_3$): δ = 17.50 [d, ^1J(PC) = 102.2 Hz, CH_3P], 22.31, 22.33, 23.51, 23.53, 23.74, 23.77, 23.87, 23.90 [s, $(CH_3)_2CH$], 47.41 [d, ^2J(PC) = 5.3 Hz, $(CH_3)_2CH$], 49.80 [d, ^2J(PC) = 4.3 Hz, $(CH_3)_2CH$], 116.11 [dd, J(PC) = 16.6 and 5.1 Hz, CH (ring)], 120.90 [q, ^1J(FC) = 320.2 Hz, CF_3], 128.78 [s, C (arom)], 129.47 [s, C (arom)], 129.66 [s, C (arom)], 132.20 [s, C (arom)], 150.31 [dd, J(PC) = 10.6 and 6.0 Hz, C (ring)], 157.97 [dd, J(PC) = 147.2 and 10.6 Hz, C=N].

$C_{35}H_{65}F_3N_6O_3P_2S_2$ (801.01)
Calcd. C 52.48 H 8.18 N 10.49
Found C 52.28 H 8.49 N 10.43

Hydrazine **27**: A large excess of water was added to **22** (0.53 g, 1.00 mmol) in pentane. After stirring for ca. 12 h at room temperature, the solvent was removed and the residue washed with THF/ether; yield 0.49 g (88%). – IR ($CDCl_3$): $\tilde{\nu}$ = 1685 cm^{-1} (C=O). – ^{31}P NMR ($CDCl_3$): δ = 53.16, 52.30 [^4J(PP) = 2.5 Hz]. – ^{1}H NMR ($CDCl_3$): δ = 1.31 [d, ^3J(HH) = 6.7 Hz, 12H, $(CH_3)_2CH$], 1.35 [d, ^3J(HH) = 6.7 Hz, 24H, $(CH_3)_2CH$], 1.41 [d, ^3J(HH) = 6.7 Hz, 12H, $(CH_3)_2CH$], 1.93 [d, ^2J(PH) = 14.7 Hz, 3H, CH_3P], 3.72 [septd, ^3J(HH) = 6.7 Hz, ^3J(PH) = 17.3 Hz, 4H, $(CH_3)_2CH$], 3.89 [septd, ^3J(HH) = 6.7 Hz, ^3J(PH) = 20.0 Hz, 4H, $(CH_3)_2CH$], 7.67 [d, ^2J(PH) = 20.5 Hz, 1H, NH], 9.60 (s, 1H, NH). – ^{13}C NMR ($CDCl_3$): δ = 14.57 [d, ^1J(PC) = 102.0 Hz, CH_3P], 22.19, 22.21, 22.92, 22.97, 23.03, 23.06, 23.73, 23.74 [s, $(CH_3)_2CH$], 47.28 [d, ^2J(PC) = 5.3 Hz, $(CH_3)_2CH$], 47.59 [d, ^2J(PC) = 1.0 Hz, $(CH_3)_2CH$], 47.76 [d, ^2J(PC) = 4.7 Hz, $(CH_3)_2CH$], 170.61 [d, ^1J(PC) = 142.7 Hz, C=O], 120.24 [q, ^1J(FC) = 319.6 Hz, CF_3].

$C_{27}H_{61}F_3N_6O_4P_2S_2$ (716.89)
Calcd. C 45.23 H 8.58 N 11.73
Found C 45.19 H 8.67 N 11.84

[Bis(diisopropylamino)thiophosphoranyl][bis(pentafluorophenyl)phosphanyl](diazo)methane **32**: A stoichiometric amount of *n*-BuLi (1.6 M in hexane) was added dropwise to 0.30 g (1.00 mmol) of [bis(diisopropylamino)thiophosphoranyl](diazo)methane in 10 ml of THF at –78°C. After stirring at this temperature for 10 min, a solution of 0.40 g (1.00 mmol) of [bis(pentafluorophenyl)]-(chloro)phosphane in 10 ml of THF was added. After warming up the solvent was removed. The residue was treated with pentane and filtrated. The diazo compound **32** was obtained as yellow crystals after purification on silica gel; yield 0.33 g (50%), mp 97–98°C, R_f = 0.7 [hexane/ether (90:10)]. – IR (toluene): $\tilde{\nu}$ = 2051 cm^{-1} (C=N$_2$). – ^{31}P NMR ($CDCl_3$): δ = 64.14, –55.15 [^2J(PP) = 141.2 and 24.0 Hz]. – ^{1}H NMR ($CDCl_3$): δ = 1.28 [d, ^3J(HH) = 6.7 Hz, 12H, $(CH_3)_2CH$], 1.39 [d, ^3J(HH) = 6.7 Hz, 12H, $(CH_3)_2CH$], 3.78 [septd, ^3J(HH) = 6.7 Hz, ^3J(PH) = 16.3 Hz, 4H, $(CH_3)_2CH$]. – ^{13}C NMR ($CDCl_3$): δ = 23.67, 23.70 [s, $(CH_3)_2CH$], 38.87 [dd, ^1J(PC) = 116.0 and 49.2 Hz, C=N$_2$], 47.95 [d, ^2J(PC) = 5.3 Hz, $(CH_3)_2CH$], 108.25 [br. s, C-*i*], 137.67 [d, ^1J(FC) = 253.0 Hz, C-*o*], 142.56 [d, ^1J(FC) = 257.5 Hz, C-*p*], 147.61 [d, ^1J(FC) = 236.4 Hz, C-*m*]. – MS (70 eV): m/z = 668 [M$^+$].

$C_{25}H_{28}F_{10}N_4P_2S$ (668.52)
Calcd. C 44.90 H 4.22 N 8.38
Found C 44.79 H 4.31 N 8.34

C-[Bis(diisopropylamino)thiophosphoranyl]-N-{(phenyl)[2,4,6-tris(trifuoromethyl)phenyl]phosphanyl}nitrilimine (**33**): A stoichiometric amount of *n*-BuLi (1.6 M in hexane) was added dropwise to 0.30 g (1.00 mmol) of [bis(diisopropylamino)thiophosphoranyl](diazo)methane in 10 ml of THF at –78°C. After stirring at this temperature for 10 min, a solution of 0.42 g (1.00 mmol) of (chloro)(phenyl)[2,4,6-tris(trifluoromethyl)phenyl]phosphane in 10 ml of THF was added. After warming up, the solvent was removed to give a brown oil which was washed several times with pentane; yield 0.57 g (82%). – IR (THF): $\tilde{\nu}$ = 2138 cm^{-1} (CNN). – ^{31}P NMR (THF): δ = 27.90 [s, P(S)], 70.60 [septd, ^4J(FP) = 41.5 Hz, P].

$C_{28}H_{35}F_9N_4P_2S$ (692.61)
Calcd. C 48.54 H 5.10 N 8.09
Found C 48.47 H 5.14 N 8.01

Hydrazine **34**: A large excess of water was added to a THF solution of nitrilimine **33** (0.67 g, 0.90 mmol). After stirring at room temperature for 48 h, the solvent was evaporated and the residue treated with pentane. After filtration and purification on silica gel, **34** was obtained as a yellow oil; yield 0.45 g (65%), R_f = 0.7 [hexane/ether (90:10)]. – IR ($CDCl_3$): $\tilde{\nu}$ = 1662 cm^{-1} (C=O), 3312 and 3381 (NH). – ^{31}P NMR ($CDCl_3$): δ = 52.89 [septd, ^4J(FP) = 42.0 Hz, ^4J(PP) = 4.2 Hz], 52.98 [d, ^4J(PP) = 4.2 Hz]. – ^{1}H NMR ($CDCl_3$): δ = 1.28 [d, ^3J(HH) = 6.9 Hz, 6H, $(CH_3)_2CH$], 1.29 [d, ^3J(HH) = 6.8 Hz, 6H, $(CH_3)_2CH$], 1.34 [d, ^3J(HH) = 6.8 Hz, 6H, $(CH_3)_2CH$], 1.35 [d, ^3J(HH) = 6.9 Hz, 6H, $(CH_3)_2CH$], 3.77 [septd, ^3J(HH) = 6.8 Hz, ^3J(PH) = 13.6 Hz, 2H, $(CH_3)_2CH$], 3.82 [septd, ^3J(HH) = 6.9 Hz, ^3J(PH) = 13.8 Hz, 2H, $(CH_3)_2CH$], 4.86 [dd, ^2J(PH) = 5.7 Hz, ^1J(HH) = 2.1 Hz, 1H, NH], 7.50 (m$_c$, 5H, C_6H_5), 8.21 [br. s, 2H, $C_6H_2(CF_3)_3$], 9.78 (br. s, 1H, NH). – ^{13}C NMR ($CDCl_3$): δ = 22.91, 22.95 [s, $(CH_3)_2CH$], 46.98 [d, ^2J(PC) = 4.9 Hz, $(CH_3)_2CH$], 47.21 [d, ^2J(PC) = 4.5 Hz, $(CH_3)_2CH$], 132.31 [m$_c$, C (arom)], 169.73 [d, ^1J(PC) = 141.5 Hz, PC=O]. – MS (70 eV): m/z = 710 [M$^+$].

$C_{28}H_{37}F_9N_4OP_2S$ (710.63)
Calcd. C 47.31 H 5.25 N 7.89
Found C 47.25 H 5.36 N 8.02

Hydrazone **35**: A stoichiometric amount of diisopropylamine (0.10 g, 1.00 mmol) was added to the nitrilimine **33** (0.69 g, 1.00 mmol) in THF at room temperature. After stirring for 1 d, the solvent was removed and the 1,3-adduct was purified on silica gel; **35** was obtained as an orange oil; yield 0.43 g (54%), R_f = 0.7 [hexane/ehter (90:10)]. – ^{31}P NMR ($CDCl_3$): δ = 67.80 [s, P(S)], 39.90 [sept, ^4J(FP) = 45.0 Hz]. – ^{1}H NMR ($CDCl_3$): δ = 1.06 [d, ^3J(HH) = 7.0 Hz, 6H, $(CH_3)_2CHNP$], 1.21 [d, ^3J(HH) = 7.0 Hz, 6H, $(CH_3)_2CHNP$], 1.34 [d, ^3J(HH) = 6.8 Hz, 6H, $(CH_3)_2CHNP$], 1.38 [d, ^3J(HH) = 6.8 Hz, 6H, $(CH_3)_2CHNP$], 1.40 [d, ^3J(HH) = 6.8 Hz, 6H, $(CH_3)_2CHNC$], 1.41 [d, ^3J(HH) = 6.8 Hz, 6H, $(CH_3)_2CHNC$], 3.66 [septd, ^3J(HH) = 6.8 Hz, 2H, $(CH_3)_2CHNC$], 4.05 [septd, ^3J(HH) = 6.8 Hz, ^3J(PH) = 13.8 Hz, 2H, $(CH_3)_2CHNP$], 4.12 [septd, ^3J(HH) = 7.0 Hz, ^3J(PH) = 13.8 Hz, 2H, $(CH_3)_2CHNP$], 7.22 [m$_c$, 5H, H (arom)], 7.97 [d, ^2J(PH) = 11.8 Hz, 1H, NH], 8.19 [s, 2H, $C_6H_2(CF_3)_3$]. – ^{13}C NMR ($CDCl_3$): δ = 21.56, 21.62, 22.68, 22.73, 23.54, 23.63, 23.73, 23.79, 24.15, 24.21 [s, $(CH_3)_2CH$], 46.90 [d, ^2J(PC) = 5.9 Hz, $(CH_3)_2CHNP$], 47.02 [d,

^2J(PC) = 6.0 Hz, $(CH_3)_2CHNP$], 49.45 [s, $(CH_3)_2CHNC$], 132.73 [m_c, C (arom)], 149.59 [dd, J(PC) = 167.0 and 20.8 Hz, C=N].

$C_{34}H_{50}F_9N_5P_2S$ (793.80) Calcd. C 51.34 H 6.35 N 8.83
Found C 51.25 H 6.42 N 8.89

CAS Registry Numbers

1: 113533-22-5 / **3a**: 129570-65-6 / **3b**: 129570-66-7 / **4a**: 133549-03-8 / **4b**: 133549-04-9 / **6**: 129570-70-3 / **10**: 129570-71-4 / **15**: 129570-67-8 / **17**: 6832-15-1 / **20**: 133549-05-0 / **21**: 133549-06-1 / **22**: 129570-69-0 / **23**: 132514-68-2 / **23** [P(V)]: 132514-77-3 / **24**: 132514-70-6 / **24** [P(V)]: 132539-28-7 / **25**: 132514-72-8 / **25** [P(V)]: 132539-29-8 / **26**: 132514-74-0 / **26** [P(V)]: 132539-30-1 / **27**: 132514-76-2 / **27** [P(V)]: 132514-78-4 / **30**: 128900-99-2 / **32**: 133549-07-2 / **33**: 133549-08-3 / **34**: 133549-09-4 / **35**: 133549-10-7 / H_2C=CHOEt: 109-92-2 / H_2C=CHPh: 100-42-5 / H_2C=$CHCO_2Me$: 96-33-3 / HC≡CPh: 536-74-3 / $(C_6F_5)_2PCl$: 5032-90-6 / MeO_2CC≡CCO_2Me: 762-42-5 / $(NC)_2C$=$C(CN)_2$: 670-54-2 / PhN_3: 622-37-7 / (chloro)(phenyl)[2,4,6-tris(trifluoromethyl)phenyl]phosphane: 133549-11-8

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