# *N*-Phosphino- and *N*-Phosphonionitrilimines: From Nucleophilic to Electrophilic 1,3-Dipoles

Francisco Palacios,*,† Jaione Pagalday,† Valérie Piquet,‡ Françoise Dahan,‡ Antoine Baceiredo,‡ and Guy Bertrand*,‡

*Departamento de Quimica Organica, Facultad de Farmacia, U.P.V./E.H.U., Apartado 450, 01080 Vitoria, Spain, and Laboratoire de Chimie de Coordination du CNRS, 205, route de Narbonne, 31077 Toulouse Cédex, France*

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*N*-[Bis(diisopropylamino)phosphino]-*C*-[bis(diisopropylamino)thioxophosphoranyl]nitrilimine (**1**) reacts with electron-poor dipolarophiles such as maleimide, methyl vinyl ketone, and 1,4-naphthoquinone via HOMO(dipole)-controlled [2+3] cycloadditions, while *N*-[bis(diisopropylamino)(methyl)-phosphonio]-*C*-[bis(diisopropylamino)thioxophosphoranyl]nitrilimine (**2a**) reacts with electron-rich dipolarophiles such as norbornadiene and ethyl *trans*-pyrrolineacrylate via LUMO(dipole)-controlled [2+3] cycloadditions. Carbon disulfide reacts with **1** via a formal [4+2] cycloaddition leading to phosphazene containing heterocycle **11** in 75% yield. Dipole **1** is cleaved by HCl, giving the corresponding (thioxophosphoranyl)diazomethane **15**, while addition of HCl to **2a** leads to hydrazonoyl chloride **16**, in 70% isolated yield. Hydrazone **17′** (95%) and phosphazine **18** (80%) are obtained by a 1,3-addition of BuLi to **1** and PhOLi to **2a**, respectively. Trimethylphosphine reacts with **2a** by a phosphine−carbene coupling reaction, giving the ylide **20** which is isolated in 75% yield.

## Introduction

Pyrazole and pyrazoline ring systems constitute not only the basic skeleton of a variety of compounds involved in dyestuffs and polymers, but also show interesting biological activities.[1] It is known that the phosphoranyl and the thioxophosphoranyl groups regulate biological functions.[2] Molecular modifications of pyrazole rings introducing organophosphorus functionalities lead to very useful agrochemical[3] products such as insecticides[4] and herbicides.[5] The most versatile synthetic route to pyrazoles and pyrazolines is the thermal 1,3-dipolar cycloaddition reaction of transient nitrilimines with dipolarophiles.[6,7] For a long time, these 1,3-dipoles were considered short-lived intermediates; however, we have recently shown that with the right set of substituents, nitrilimines can exist as stable compounds in the solid state and in solution.[8] In addition to stabilizing effects, the nature of the substituents can also modify the behavior of nitrilimines. In Sustmann's classification nitrilimines belong to the type II dipoles, which implies that HOMO(dipole)/LUMO(dipolarophile) and HOMO(dipolarophile)/LUMO(dipole) interactions are about equally important.[9] Consequently, nitrilimines can behave as both nucleophiles and electrophiles toward dipolarophiles. This statment agrees well with the experimental results observed for transient nitrilimines,[6] but we have found that this amphiphilic character is not so obvious for the stable nitrilimines. The presence of the phosphino substituent on the nitrogen atom confers nitrilimine **1** with a nucleophilic character thus favoring HOMO(dipole)-controlled cycloadditions,[10] while the *N*-phosphonionitrilimines **2** present a strong electrophilic character involving LUMO(dipole)-controlled cycloadditions (Scheme 1).[11] In connection with our interest in the synthesis of five[12]- and six[13]-membered nitrogen heterocycles, we report here some examples of intermolecular cycloaddition reactions of stable nitrilimines **1** and **2** with a wide range of dipolarophiles. The difference in behavior of **1** and **2** is also illustrated by further types of reaction.

## Results and Discussion

We first explored the reactivity of nitrilimine **1** with electron-poor dipolarophiles. Maleimide reacts with **1**

† U.P.V./E.H.U.

‡ Laboratoire de Chimie de Coordination du CNRS.

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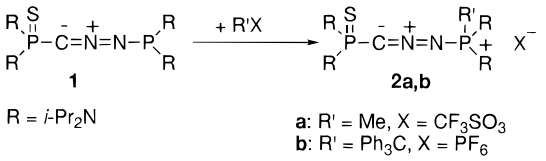
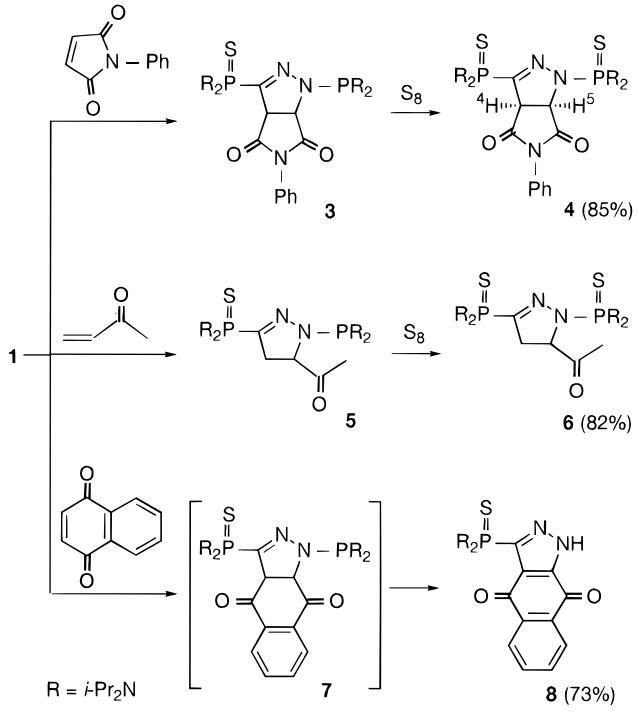
**Scheme 1**



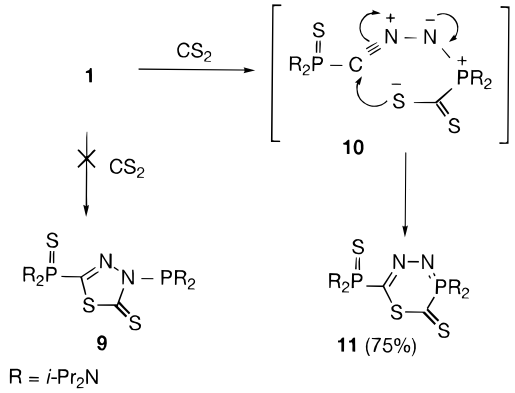

**Scheme 2**




under mild reaction conditions (25 °C, 6 h, THF) leading to the pyrazoline **3**, which was isolated as **4** (85% yield) after treatment with 1 equiv of elemental sulfur (Scheme 2). The stereoselective *cis* addition of maleimide to **1** is shown by the *syn* configuration of the bicyclic compound **4** [$^3J_{H^4-H^5}$ = 10.3 Hz]. Nitrilimine **1** reacts with the methyl vinyl ketone at room temperature (3 h), affording the pyrazoline **5** which, after addition of elemental sulfur, led to the *C*, *N*-bis(thioxophosphoranyl)pyrazoline **6** (82% yield), indicating that the cycloaddition was completely regioselective. Treatment of **1** with 1,4-naphthoquinone followed by addition of elemental sulfur afforded the pyrazole **8** (73% yield), which results from the spontaneous aromatization of the initially formed pyrazoline **7**, with subsequent cleavage of the phosphorus−nitrogen linkage (probably due to traces of water). It is noteworthy that heterocycles derived from maleimides are used in polymer synthesis,[14] while quinone derivatives can exhibit anticancer activity.[15]

The formation of thiadiazoline derivatives are usually observed on treating carbon−sulfur double-bond-containing dipolarophiles with transient nitrilimines.[16] Surprisingly, when carbon disulfide was added to nitrilimine **1** at room temperature, formation of the expected thiadiazoline **9** was not observed, but the six-membered heterocycle **11** (75% yield) was isolated instead (Scheme 3). Phosphazene containing heterocycle **11** was characterized

**Scheme 3**




on the basis of its spectroscopic data. The $^{31}$P NMR spectrum showed two different resonances at $\delta$ +61.3 and +3.6 ppm, the high-field chemical shift being consistent with the cyclic phosphazenyl group and not with a phosphino group.[11a,17] Moreover, in the $^{13}$C NMR spectrum the C=N carbon atom appeared at $\delta$ = 141.1 ppm as a well-resolved doublet of doublets ($^1J_{PC}$ = 158.6 and $^3J_{PC}$ = 49.4 Hz). Formation of six-membered heterocycle **11** is one of the very rare examples[11a] showing the formal 1,4-dipolar behavior of **1**.

Since nitrilimine **1** failed to react with electron-rich dipolarophiles, and in order to generalize the synthetic use of stable nitrilimines, the reactions of *N*-phosphonionitrilimine **2** were explored. *N*-phosphonionitrilimine **2a** was easily obtained in one step by adding the stoichiometric amount of methyl trifluoromethanesulfonate to the *N*-phosphinonitrilimine **1**.[11b] In the same way, derivative **2b** was prepared, in 85% yield, using triphenylcarbenium hexafluorophosphate as electrophile. The $^{13}$C NMR signal of the dipole-carbon appeared in the usual range (69.2 ppm, dd, $J_{PC}$ = 103.2 and 10.1 Hz) and an AX system (29.6 and 42.6, $^4J_{PP}$ = 5.7 Hz) was present in the $^{31}$P NMR spectrum. As expected for a nitrilimine with an electron-withdrawing substituent, the CNN stretching vibration for **2b** appears at a higher frequency (2168 cm$^{-1}$) compared to **1** (2040 cm$^{-1}$)[10] (Scheme 1).

Electron-withdrawing substituents such as phosphonio groups should confer an electrophilic character to nitrilimines **2** and hence invoke LUMO(dipole)-controlled cycloadditions. Therefore, reactivity of nitrilimine **2a** with electron-rich dipolarophiles such as norbornadiene and enamines was explored. It is noteworthy that these reagents have been especially used in inverse electron demand cycloaddition processes.[18,19] The reaction of nitrilimine **2a** with an excess of norbornadiene in THF at room temperature (48 h) led to the formation of cycloadduct **12** in a stereoselective fashion, in contrast to transient nitrilimines which gave a mixture of exo and endo isomers.[19a,b] The value of the vicinal coupling constant ($^3J_{H^4-H^5}$ = 9.2 Hz) and the absence of coupling between these protons and $H^A$ and $H^B$ were consistent with the exo structure.[19c] Similarly, *N*-phosphonionitrilimine **2a** reacts with ethyl *trans*-pyrroline acrylate leading regio- and stereoselectively to the substituted pyra-

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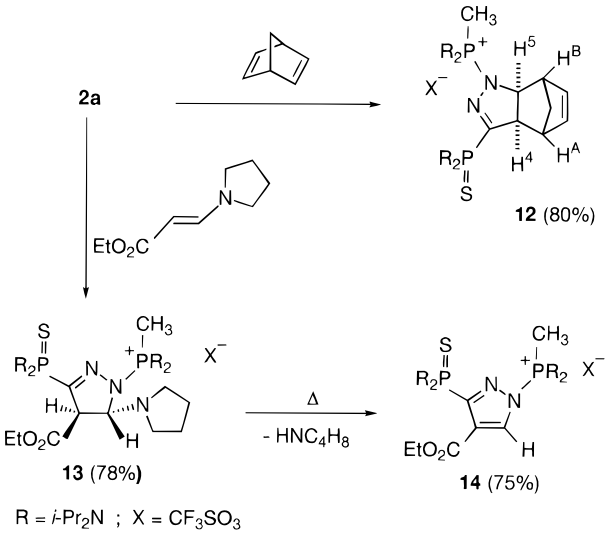
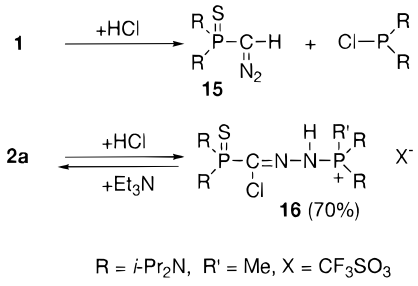
**Scheme 4**




**Scheme 5**

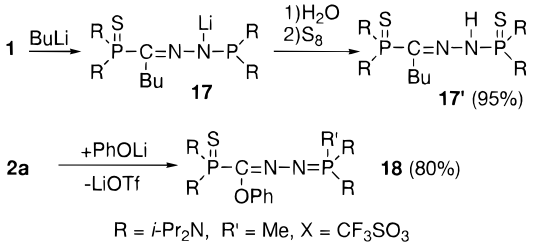



zoline **13** (78% yield). Heating heterocycle **13** at 50 °C (15h) gave pyrazole **14** in 75% yield (Scheme 4). Spectroscopic data were consistent with the proposed structure, in which the pyrazole is substituted by the ethoxycarbonyl group in the 4-position, the resonance attributed to $H^5$ appearing at 8.89 ppm. Interestingly, ethyl *trans*-pyrrolineacrylate, can be considered as the synthetic equivalent of ethyl propiolate,[18] yet has the added advantage of the regioselectivity associated with its reactions.[20]

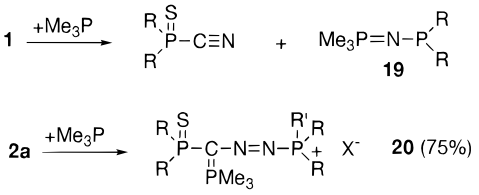
Reagents possessing acidic protons led to the cleavage of the P−N bond in the case of nitrilimine **1**. Indeed, addition of 1 equiv of an ethereal solution of HCl gives rise to the formation of bis[(diisopropylamino)thioxophosphoranyl]diazomethane (**15**) along with the corresponding amount of chlorophosphine. In marked contrast, nitrilimine **2a** reacts with HCl by a 1,3-addition process affording hydrazonoyl chloride **16**, in 70% isolated yield. Compound **16** was fully characterized including an X-ray diffraction study.[21] Notably, elimination of hydrogen chloride occurs by adding a stoichiometric amount of tertiary amine ($Et_3N$), giving back nitrilimine **2a**, in near quantitative yield (Scheme 5).

Nitrilimine **1** reacts via a 1,3-addition process with butyllithium leading to the formation of the hydrazone salt **17**, which was characterized in solution by $^{31}P$ NMR

**Scheme 6**




**Scheme 7**




spectroscopy, and conversion by hydrolysis and addition of elemental sulfur, to the *C*,*N*-bis(thioxophosphoranyl)-hydrazone (**17′**, 95% yield). Similarly, addition of 1 equiv of lithium phenoxide to nitrilimine **2a** led to phosphazine **18** as a colorless oil in 80% yield (Scheme 6).

The difference in the reactivity of dipoles **1** and **2a** is also illustrated by the results observed in the addition of trimethylphosphine. Nitrilimine **1** reacts with $Me_3P$ at −78 °C with cleavage of the phosphorus−nitrogen bond leading to the corresponding bis[(diisopropylamino)-thioxophosphoranyl]nitrile[22] and the (phosphino)iminophosphorane **19**. Due to the high sensitivity of compound **19**, it could only be characterized in solution by $^{31}P$ NMR spectroscopy (AX system, +76.2, +4.8 ppm, $^2J_{PP} = 157$ Hz). In contrast, under the same experimental conditions, nitrilimine **2a** reacts with trimethylphosphine giving **20**, which still features the CNN skeleton. Formally, the formation of phosphorus ylide **20** involves a coupling reaction between $Me_3P$ and the carbenic form of the dipole **2a**. The presence of three different phosphorus atoms in **20** is indicated by the $^{31}P$ NMR [PS 61.5 ($J_{PP}$ = 102.0 and 4.5 Hz); $P^+$ +52.0 ($J_{PP}$ = 4.5 and 4.7 Hz); MeP +5.7 ($J_{PP}$ = 102.0 and 4.7 Hz)] and the $^{13}C$ NMR spectra [CNN 126.4, ddd ($J_{PC}$ = 156.8, 47.9 and 31.8 Hz)] (Scheme 7).

## Conclusion

Stable nitrilimines **1** and **2** have complementary reactivity in 1,3-cycloaddition processes and can thus be used in conjunction with a variety of dipolarophiles, to gain an easy entry to a wide range of phosphorus substituted five- and six-membered heterocyclic compounds. In contrast to transient nitrilimines, **1** and **2** undergo regio- and stereoselective cycloaddition reactions. The striking difference in reactivity between **1** and **2** is confirmed by the results observed with both electrophilic as well as ionic or neutral nucleophilic reagents.

## Experimental Section

**General.**[23] All experiments were performed under an atmosphere of dry argon or nitrogen. Melting points are uncorrected.

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**Nitrilimine 2b.** A $CH_2Cl_2$ solution (5 mL) of triphenylcarbenium hexafluorophosphate (0.19 g, 0.48 mmol) was added to a dichloromethane solution (10 mL) of *N*-phosphinonitrilimine **1** (0.26 g, 0.48 mmol) at −78 °C. After 30 min at low temperature, the mixture was allowed to warm to rt, $^{31}$P NMR spectroscopy indicating the quantitative formation of *N*-phosphonionitrilimine **2b**. Evaporation of the solvent led to the isolation of **2b** as a spectroscopically pure yellow oil (0.38 g, 85% yield): $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.33 (d, 24 H, $J_{HH}$ = 6.9 Hz), 1.36 (d, 24 H, $J_{HH}$ = 6.9 Hz), 3.85 (m, 8 H), 7.06−7.29 (m, 15 H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 22.3, 22.9, 23.7, 23.8, 47.1 (d, $J_{PC}$ = 5.6 Hz), 48.6 (d, $J_{PC}$ = 3.0 Hz), 68.1 (d, $J_{PC}$ = 100.1 Hz), 69.2 (dd, $J_{PC}$ = 103.2 and 10.1 Hz), 127.8, 128.3, 130.2 (d, $J_{PC}$ = 3.7 Hz), 132.1 (d, $J_{PC}$ = 13.6 Hz); $^{31}$P NMR (32 MHz, $CDCl_3$) $\delta$ −144.9 (sept, $J_{PF}$ = 712.1 Hz), 29.6 (d, $J_{PP}$ = 5.7 Hz), 42.6 (d, $J_{PP}$ = 5.7 Hz); IR ($CH_2Cl_2$) 2168 cm$^{-1}$. Anal. Calcd for $C_{44}H_{71}N_6F_6P_3S$: C, 57.25; H, 7.75; N, 9.10. Found: C, 57.30; H, 7.79; N, 9.15.

**2,4-Bis[bis(diisopropylamino)thioxophosphoranyl]-7-phenyl-2,3,7-triazabicyclo[3.3.0.]octane (4).** To a THF solution (5 mL) of nitrilimine **1** (1.60 g, 3 mmol) was added a THF solution (10 mL) of *N*-phenylmaleimide (0.52 g, 3 mmol). The mixture was stirred for 6 h at rt, and then sulfur (0.11 g, 3.3 mmol) was added to the mixture. After the mixture was stirred for 2 h at rt, the solvent was removed under vacuum and the crude residue was purified by flash column chromatography (silica gel) with hexane as eluent to give pyrazoline **4** as an oil, which was recrystallized from pentane as a white solid (1.88 g, 85% yield): mp 136−137 °C dec; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.31−1.45 (m, 48H), 3.75 (m, 6H), 4.11 (m, 2H), 4.42 (d, 1 H, $J_{HH}$ = 10.3 Hz), 6.05 (dd, 1 H, $J_{HH}$ = 10.3 Hz, $J_{PH}$ = 4.6 Hz), 7.26−7.42 (m, 5H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 23.3−24.9, 47.9 (d, $J_{PC}$ = 5.5 Hz), 48.1 (d, $J_{PC}$ = 6.0 Hz), 48.3 (d, $J_{PC}$ = 5.5 Hz), 49.0 (d, $J_{PC}$ = 6.0 Hz), 54.5 (dd, $J_{PC}$ = 19.9 Hz, $J_{PC}$ = 2.3 Hz), 65.4 (dd, $J_{PC}$ = 11.1 Hz, $J_{PC}$ = 2.0 Hz), 126.0−131.9, 148.8 (dd, $J_{PC}$ = 151.1 Hz, $J_{PC}$ = 7.1 Hz), 170.4 (d, $J_{PC}$ = 2.0 Hz), 173.4; $^{31}$P NMR (150 MHz, $CDCl_3$) $\delta$ 56.8, 64.7; IR (KBr) 1733 cm$^{-1}$; MS (El) *m*/*z* 739 ($M^+$). Anal. Calcd for $C_{35}H_{63}N_7O_2P_2S_2$: C, 56.81; H, 8.58; N, 13.25. Found: C, 56.89; H, 8.55; N, 13.28.

**1,3-Bis[bis(diisopropylamino)thioxophosphoranyl]-5-acetylpyrazoline (6).** Reaction of methyl vinyl ketone (0.21 g, 3 mmol) with nitrilimine **1** (1.60 g, 3 mmol) for 3 h and addition of sulfur (0.11 g, 3.3 mmol) (as described above for compound **4**) gave, after purification by column chromatography with hexane as eluent, the pyrazoline **6** as a white solid (1.56 g, 82% yield): mp 84−85 °C dec; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.19−1.36 (m, 48 H), 2.23 (s, 3H), 2.77−2.83 (m, 2 H), 3.59−4.17 (m, 8 H), 4.89 (m, 1 H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 22.7−24.3, 28.0, 40.4 (dd, $J_{PC}$ = 24.7 Hz, $J_{PC}$ = 5.0 Hz), 47.3 (d, $J_{PC}$ = 5.5 Hz), 47.4 (d, $J_{PC}$ = 6.0 Hz), 47.8 (d, $J_{PC}$ = 5.5 Hz), 47.9 (d, $J_{PC}$ = 6.0 Hz), 65.3 (dd, $J_{PC}$ = 11.6 Hz, $J_{PC}$ = 3.5 Hz), 149.5 (dd, $J_{PC}$ = 149.3 Hz, $J_{PC}$ = 8.8 Hz), 205.8; $^{31}$P NMR (150 MHz, $CDCl_3$) $\delta$ 58.5 (d, $J_{PP}$ = 3.8 Hz), 62.7 (d, $J_{PP}$ = 3.8 Hz); IR (KBr) 1735, 1276 cm$^{-1}$; MS (El) *m*/*z* 636 ($M^+$). Anal. Calcd for $C_{29}H_{62}N_6OP_2S_2$: C, 54.69; H, 9.81; N, 13.19. Found: C, 54.79; H, 9.80; N, 13.23.

**3-[Bis(diisopropylamino)thioxophosphoranyl]naphthoquinoyl[2,3-d]pyrazole (8).** Reaction of 1,4-naphthoquinone (0.47 g, 3 mmol) with nitrilimine **1** (1.60 g, 3 mmol) for 2 h (as described above for compound **4**) gave, after purification by column chromatography with $Et_2O$/hexane (1:5) as eluent, the pyrazole **8** as a green solid (1.01 g, 73% yield): mp 230−231 °C dec; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.18 (d, 12 H, $J_{HH}$ = 6.9 Hz), 1.36 (d, 12 H, $J_{HH}$ = 6.9 Hz), 1.44 (s, 1 H), 4.05 (m, 4 H), 7.71−8.29 (m, 4 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 23.5−24.0, 48.1 (d, $J_{PC}$ = 6.5 Hz), 120.4 (d, $J_{PC}$ = 7.6 Hz), 124.5 (d, $J_{PC}$ = 4.5 Hz), 127.2, 127.6, 133.6, 133.7, 134.2, 135.0, 141.7 (d, $J_{PC}$ = 119.4 Hz), 179.1, 179.2; $^{31}$P NMR (150 MHz, $CDCl_3$) $\delta$ 54.6; IR (KBr) 3282, 1680 cm$^{-1}$; MS (El) *m*/*z* 460 ($M^+$). Anal. Calcd for $C_{23}H_{33}N_4O_2PS$: C, 59.98; H, 7.22; N, 12.16. Found: C, 59.94; H, 7.20; N, 12.14.

**2-[Bis(diisopropylamino)thioxophosphoranyl]-5,5-bis(diisopropylamino)-6-thioxo-1,6-dihydro-1,3,4,5-thiadiazaphosphinine (11).** Reaction of carbon disulfide (0.23 g, 3 mmol) with nitrilimine **1** (1.60 g, 3 mmol) for 4 h (as described above for compound **4**) gave, after purification by column chromatography with hexane as eluent, the thiadiazaphosphinine **11** as a brown solid (1.37 g, 75% yield): mp 85−86 °C dec; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.15 (d, 6 H, $J_{HH}$ = 6.9 Hz), 1.21 (d, 6 H, $J_{HH}$ = 6.9 Hz), 1.26 (d, 6 H, $J_{HH}$ = 7.0 Hz), 1.31 (m, 30 H), 3.72 (m, 4 H), 3.94 (m, 4 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 22.5−24.0, 47.4 (d, $J_{PC}$ = 5.5 Hz), 47.5 (d, $J_{PC}$ = 5.5 Hz), 141.1 (dd, $J_{PC}$ = 158.6 Hz, $J_{PC}$ = 49.4 Hz), 214 (dd, $J_{PC}$ = 73.0 Hz, $J_{PC}$ = 9.3 Hz); $^{31}$P NMR (150 MHz, $CDCl_3$) $\delta$ 3.6, 61.3; MS (El) *m*/*z* 610 ($M^+$). Anal. Calcd for $C_{26}H_{56}N_6P_2S_3$: C, 51.12; H, 9.24; N, 13.76. Found: C, 51.10; H, 9.14; N, 13.74.

**[4,5-(4-Cyclopentane-1,3-ylene)[3-[Bis(diisopropylamino)thioxophosphoranyl]-2-pyrazolinyl]bis(diisopropylamino)methylphosphonium Triflate (12).** Reaction of 2,5-norbornadiene (1.66 g, 18 mmol) with nitrilimine **2a** (2.09 g, 3 mmol) for 48 h (as described above for compound **4**) gave, after recrystallization from THF/$Et_2O$, the cycloadduct **12** (1.90 g, 80% yield): mp 147−148 °C dec; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.34 (m, 48 H), 1.45 (d, 1 H, $J_{HH}$ = 9.6 Hz), 1.66 (d, 1 H, $J_{HH}$ = 9.6 Hz), 2.34 (d, 3 H, $J_{PH}$ = 13.9 Hz), 3.14 ($s_{broad}$, 1 H), 3.80 (m, 9 H), 4.04 ($s_{broad}$, 1 H), 4.27 (d, 1 H, $J_{HH}$ = 9.2 Hz), 6.10 (dd, 1 H, $J_{HH}$ = 5.7 Hz, $J_{HH}$ = 3.1 Hz), 6.29 (dd, 1 H, $J_{HH}$ = 5.7 Hz, $J_{HH}$ = 3.1 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 16.0 (d, $J_{PC}$ = 103.2 Hz), 22.4−24.3, 42.9, 47.6 (d, $J_{PC}$ = 6.0 Hz), 48.2 (d, $J_{PC}$ = 5.0 Hz), 48.4 (d, $J_{PC}$ = 5.5 Hz), 48.6 (d, $J_{PC}$ = 6.0 Hz), 50.5, 62.3 (dd, $J_{PC}$ = 20.9 Hz, $J_{PC}$ = 4.8 Hz), 68.8 (t, $J_{PC}$ = 5.5 Hz), 77.0, 120.6 (d, $J_{FC}$ = 320.8 Hz), 135.6, 140.8, 159.6 (dd, $J_{PC}$ = 135.3 and 11.9 Hz); $^{31}$P NMR (150 MHz, $CDCl_3$) $\delta$ 52.6, 57.1; MS (El) *m*/*z* 576 ($M^+ - CF_3SO_3 - C_5H_7$). Anal. Calcd for $C_{34}H_{67}F_3N_6O_3P_2S_2$: C, 51.63; H, 8.54; N, 10.62. Found: C, 51.70; H, 8.51; N, 10.64.

**[[3-[Bis(diisopropylamino)thioxophosphoranyl]-4-(ethoxycarbonyl)-5-pyrrolidinyl]-2-pyrazolinyl]bis(diisopropylamino)methylphosphonium Triflate (13).** To a THF solution (10 mL) of nitrilimine **2a** (2.09 g, 3 mmol) was added a toluene solution (15 mL) of ethyl *trans*-2-pyrrolidineacrylate (0.51 g, 3 mmol), and the mixture was stirred for 52 h at rt. Evaporation of the solvent under reduced pressure afforded an oil which was recrystallized from $Et_2O$ to give **13** as a white solid (2.03 g, 78% yield): mp 89−90 °C dec; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.27 (m, 51 H), 1.75 (m, 2 H), 1.82 (m, 2 H), 2.27 (d, 3 H, $J_{PH}$ = 14.2 Hz), 2.54 (m, 4 H), 3.77 (m, 8 H), 4.14 (q, 2 H, $J_{HH}$ = 7.2 Hz), 4.42 (t, 1 H, $J_{HH}$ = $J_{PH}$ = 2.9 Hz), 5.10 (t, 1 H, $J_{HH}$ = $J_{PH}$ = 2.9 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 15.9 (d, $J_{PC}$ = 99.7 Hz), 18.4, 23.3, 23.4−24.1, 46.7, 47.7 (d, $J_{PC}$ = 5.5 Hz), 47.8 (d, $J_{PC}$ = 6.0 Hz), 48.6 (d, $J_{PC}$ = 5.5 Hz), 49.0 (d, $J_{PC}$ = 5.5 Hz), 55.1 (dd, $J_{PC}$ = 19.6 and 5.0 Hz), 62.4, 80.6 (dd, $J_{PC}$ = 7.4 and 3.4 Hz), 120.6 (d, $J_{FC}$ = 319.8 Hz), 157.9 (dd, $J_{PC}$ = 135.8 and 9.9 Hz), 170.3; $^{31}$P NMR (150 MHz, $CDCl_3$) $\delta$ 52.0, 56.4; IR (KBr) 1731, 1260 cm$^{-1}$. Anal. Calcd for $C_{36}H_{74}F_3N_7O_5P_2S_2$: C, 49.81; H, 8.59; N, 11.29. Found: C, 49.89; H, 8.57; N, 11.33.

**[3-[Bis(diisopropylamino)thioxophosphoranyl]-4-(ethoxycarbonyl)pyrazolyl]bis(diisopropylamino)-methylphosphonium Triflate (14).** A toluene solution (15 mL) of pyrazoline **13** (1.73 g, 2 mmol) was heated at 50 °C for 15 h. Evaporation of solvent under reduced pressure afforded an oil which was recrystallized from THF/$Et_2O$ to give **14** as a white solid (1.19 g, 75% yield): mp 210−211 °C dec; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.24 (m, 15 H), 1.29 (d, 12 H, $J_{HH}$ = 7.0 Hz), 1.34 (d, 12 H, $J_{HH}$ = 6.9 Hz), 1.39 (d, 12 H, $J_{HH}$ = 6.7 Hz), 2.88 (d, 3 H, $J_{PH}$ = 14.2 Hz), 3.84−4.02 (m, 8 H), 4.34 (q, 2 H, $J_{HH}$ = 7.2 Hz), 8.89 ($s_{broad}$, 1 H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 14.1, 16.5 (d, $J_{PC}$ = 102.2 Hz), 22.2−24.1, 47.9 (d, $J_{PC}$ = 6.0 Hz), 49.7 (d, $J_{PC}$ = 5.0 Hz), 65.8, 120.7 (d, $J_{FC}$ = 320.8 Hz), 122.9, 141.3, 157.9 (dd, $J_{PC}$ = 136.7 and 8.8 Hz), 161.1; $^{31}$P NMR (150 MHz, $CDCl_3$) $\delta$ 49.7, 59.9; IR (KBr) 1743, 1273 cm$^{-1}$; MS (El) *m*/*z* 647 ($M^+ - CF_3SO_3$). Anal. Calcd for $C_{32}H_{65}F_3N_6O_5P_2S_2$: C, 48.23; H, 8.22; N, 10.54. Found: C, 48.18; H, 8.20; N, 10.57.

**Cleavage of Nitrilimine 1.** A 1 M ether solution of HCl (0.48 mL, 0.48 mmol) was added, at −78 °C, to a $CH_2Cl_2$ solution (10 mL) of *N*-phosphinonitrilimine **1** (0.26 g, 0.48 mmol). After 30 min at low temperature, the solution was allowed to warm to rt, and $^{31}$P NMR spectroscopy indicated

the quantitative formation of [bis(diisopropylamino)thioxophosphoranyl]diazomethane (**15**)[10] and bis(diisopropylamino)-chlorophosphine.

**Chlorohydrazone 16.** A 1 M ether solution of HCl (0.07 mL, 0.07 mmol) was added to a $CH_2Cl_2$ solution (5 mL) of *N*-phosphonionitrilimine **2a** (0.05 g, 0.07 mmol) at rt. After the solution was stirred 30 min, the solvent was removed under vacuum leading to compound **16** as a white powder (0.04 g, 70% yield): mp 116−120 °C; $^{31}$P NMR (32 MHz, $CDCl_3$) $\delta$ 49.7 (d, $J_{PP}$ = 3.3 Hz), 61.6 (d, $J_{PP}$ = 3.3 Hz); $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.27 (d, 12 H, $J_{HH}$ = 6.4 Hz), 1.31 (d, 12 H, $J_{HH}$ = 6.4 Hz), 1.33 (d, 12 H, $J_{HH}$ = 6.8 Hz), 1.36 (d, 12 H, $J_{HH}$ = 6.8 Hz), 2.26 (d, 3 H, $J_{HH}$ = 14.6 Hz), 3.48 (m, 4 H), 3.75 (m, 4 H), 8.83 (d, 1 H, $J_{PH}$ = 33.0 Hz); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 15.8 (d, $J_{PC}$ = 77.3 Hz), 22.4, 23.1, 23.9, 24.1, 48.1 (d, $J_{PC}$ = 5.5 Hz), 48.2 (d, $J_{PC}$ = 5.1 Hz), 120.9 (q, $J_{FC}$ = 320.8 Hz), 127.7 (dd, $J_{PC}$ = 156.7 and 15.6 Hz). Anal. Calcd for $C_{27}H_{60}N_6O_3F_3P_2S_2Cl$: C, 44.10; H, 8.22; N, 11.43. Found: C, 44.04; H, 8.17; N, 11.48.

**Hydrazones 17 and 17′.** To a THF solution (10 mL) of *N*-phosphinonitrilimine **1** (0.25 g, 0.47 mmol) was added at −78 °C, 1.1 equiv of 1.6 M hexane solution of BuLi (0.32 mL, 0.52 mmol). After the solution was warmed to rt, the lithium salt **17** was characterized in solution by $^{31}$P NMR: $\delta$ 80.6 (d, $J_{PP}$ = 4.9 Hz), 86.4 (d, $J_{PP}$ = 4.9 Hz). To this solution was added wet THF (5mL) and 1 equiv of sulfur (0.015 g, 0.47 mmol), and the reaction mixture was stirred overnight at rt. Filtration of the salts and evaporation of the solvent led to derivative **17′** as a yellow oil (0.27 g, 95% yield): $^{31}$P NMR (32 MHz, $CDCl_3$) $\delta$ 62.1 (d, $J_{PP}$ = 3.2 Hz), 65.4 (d, $J_{PP}$ = 3.2 Hz); $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 0.93 (t, 3 H, $J_{HH}$ = 7.3 Hz), 1.28 (d, 12 H, $J_{HH}$ = 6.9 Hz), 1.32 (d, 12 H, $J_{HH}$ = 6.9 Hz), 1.36 (d, 24 H, $J_{HH}$ = 6.9 Hz), 1.69 (m, 2 H), 2.53 (m, 2 H), 3.87 (m, 8 H), 6.42 (d, 1 H, $J_{PH}$ = 21.8 Hz); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 13.6, 22.6 (d, $J_{PC}$ = 2.6 Hz), 23.3, 23.7, 23.9 (d, $J_{PC}$ = 3.1 Hz), 24.1 (d, $J_{PC}$ = 2.8 Hz), 28.3, 28.8 (d, $J_{PC}$ = 33.6 Hz), 47.1 (d, $J_{PC}$ = 5.6 Hz), 47.3 (d, $J_{PC}$ = 5.5 Hz), 152.9 (dd, $J_{PC}$ = 149.9 and 14.7 Hz). Anal. Calcd for $C_{29}H_{66}N_6P_2S_2$: C, 55.74; H, 10.64; N, 13.45. Found: C, 55.80; H, 10.49; N, 13.40.

**Phosphazine 18.** To a THF solution (15 mL) of *N*-phosphonionitrilimine **2a** (0.30 g, 0.43 mmol) was added at −78 °C, 1 equiv of PhOLi (0.045 g, 0.43 mmol). After warming to rt the solvent was removed under vacuum, and the lithium salts were precipitated by adding pentane (10 mL) to the residue. Evaporation of pentane led to phosphazine **18** as a colorless oil (0.27 g, 80% yield): $^{31}$P NMR (32 MHz, $CDCl_3$) $\delta$ 48.9 (d, $J_{PP}$ = 1.7 Hz), 60.2 (d, $J_{PP}$ = 1.7 Hz); $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.02 (d, 12 H, $J_{HH}$ = 6.8 Hz), 1.08 (d, 12 H, $J_{HH}$ = 6.8 Hz), 1.18 (d, 12 H, $J_{HH}$ = 6.8 Hz), 1.20 (d, 12 H, $J_{HH}$ = 6.8 Hz), 1.65 (d, 3 H, $J_{HH}$ = 13.6 Hz), 3.45 (sept d, 4 H, $J_{HH}$ = 6.8 Hz, $J_{PH}$ = 16.7 Hz), 3.98 (sept d, 4 H, $J_{HH}$ = 6.8 Hz, $J_{PH}$ = 15.8 Hz), 6.75−7.01 (m, 5 H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 15.3 (d, $J_{PC}$ = 78.6 Hz), 22.5, 22.8, 23.9, 24.0, 45.6 (d, $J_{PC}$ = 4.4 Hz), 47.4 (d, $J_{PC}$ = 5.8 Hz), 116.1,119.8, 128.4, 140.6 (dd, $J_{PC}$ = 217.9 and 46.4 Hz), 157.3 (d, $J_{PC}$ = 2.9 Hz). Anal. Calcd for $C_{32}H_{64}N_6OP_2S$: C, 59.78; H, 10.03; N, 13.07. Found: C, 59.62; H, 10.12; N, 13.01.

**Addition of Trimethylphosphine to Nitrilimine 2a.** To a THF solution (15 mL) of nitrilimine **2a** (0.30 g, 0.43 mmol) was added at −78 °C a THF solution (1 M) of $Me_3P$ (0.43 mL, 0.43 mmol). After the solution was warmed to rt the solvent was removed under vacuum, and the residue was washed several times with pentane. Compound **20** was obtained as a yellow oil: (0.24 g, 75% yield); $^{31}$P NMR (32 MHz, $CDCl_3$) $\delta$ +61.5 [dd, $J_{PP}$ = 102.0 and 4.5 Hz, PS], +52.0 [dd, $J_{PP}$ = 4.5 and 4.7 Hz, $P^+$], +5.7 [dd, $J_{PP}$ = 102.0 and 4.7 Hz, PMe]; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 1.14 (d, 12 H, $J_{HH}$ = 6.7 Hz), 1.21 (d, 12 H, $J_{HH}$ = 6.7 Hz), 1.30 (d, 12 H, $J_{HH}$ = 6.7 Hz), 1.32 (d, 12 H, $J_{HH}$ = 6.7 Hz), 1.86 (d, 3 H, $J_{PH}$ = 13.4 Hz), 2.26 (d, 9 H, $J_{PH}$ = 14.1 Hz), 3.45 (m, 4 H), 3.77 (m, 4 H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 13.8 (d, $J_{PC}$ = 54.0 Hz), 14.9 (d, $J_{PC}$ = 82.8 Hz), 22.3−23.6, 46.4 (d, $J_{PC}$ = 4.3 Hz), 47.9 (d, $J_{PC}$ = 5.7 Hz), 120.9 (q, $J_{CF}$ = 320.8 Hz), 126.4 (ddd, $J_{PC}$ = 156.8, 47.9 and 31.8 Hz). Anal. Calcd for $C_{30}H_{68}F_3N_6O_3P_3S_2$: C, 46.50; H, 8.84; N, 10.84. Found: C, 46.65; H, 8.69; N, 10.70.

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