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Stable N-Phosphorylated 1,2,4-Triazol-5-ylidenes: Novel Ligands for Metal Complexes

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Supporting Information

ABSTRACT: Synthetic routes to novel N-phosphorylated 1,2,4-triazolium salts have been developed. Treatment of the specified salts with strong base produces new stable N-phosphorylated 1,2,4-triazol-5-ylidenes, which add Se in two stages (first at the carbene carbon and then at phosphorus) and rearrange to C-phosphorylated triazoles with heating. The capacity of such N-phosphorylated triazol-5-ylidenes to act as bidentate ligands toward transition-metal centers has also been demonstrated; in particular, the formation of two dinuclear silver carbene complexes is described herein. The structures of one representative carbene and of one carbene complex were determined by an X-ray study.

INTRODUCTION

N-Heterocyclic carbenes (NHCs) have established themselves as versatile and powerful ligands for homogeneous catalysis. In addition to numerous reviews, a few books devoted to NHCs have been published recently.[1] Overwhelming attention has been paid to imidazol-2-ylidenes and imidazolidin-2-ylidenes; in these ligands, changing the wingtip substituents allows the fine tuning of steric properties, whereas introducing substituents at the 4- and/or 5-positions allows significant influence over the basicity. Nevertheless, research toward alternative NHC ligand scaffolds has also flourished in recent times, as well as research toward multidentate ligands involving NHCs together with other coordinating moieties.[2]

Although carbenes based on the 1,2,4-triazole scaffold, where an additional nitrogen atom is present in the heterocyclic ring, have received relatively little attention, some promising results have been achieved (Figure 1). The most famous among the 1,2,4-triazolylidenes is 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene (TPT), which was first prepared and studied by Enders et al.[3−7] The ubiquitous TPT was used for synthesis of a series of complexes with Pd,[8−10] Ru,[11,12] Pt,[13] Ir,[14] and group 6 metals.[15]

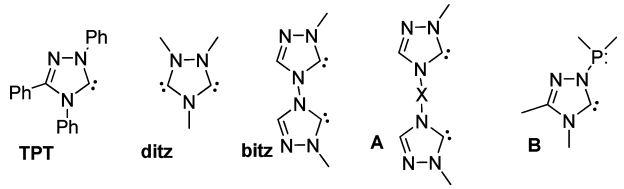

Figure 1. The most popular 1,2,4-triazolylidenes (TPT, ditz, bitz, A) and the subject of this study (B).

Another promising bis-carbene of the 1,2,4-triazole series, namely 1,2,4-trimethyltriazol-3,5-diylidene (ditz), was reported by Bertrand et al. as a building block for organometallic polymer synthesis.[16] Recently, coordination of ditz with a series of transition metals was reported, which affords discrete homo- and heterobinuclear complexes.[17−22] Some of these complexes proved to be active catalysts in three different tandem processes.

Bitriazol-2-ylidene (bitz), which has a planar structure due to a direct N−N bond linking the azole rings, has already been proven to be a potential ligand for broad applications in transition-metal chemistry.[23,24]

Additional dicarbene ligands were proposed, in which two triazolylidene moieties were connected by a short linker, mainly a methylene group (**A**). Ligands of this type were used for the synthesis of complexes with Rh, Pd, Cr, and W.[25−27]

We have recently reported that the reaction of 1-alkylimidazoles with phosphorus(III) halides produces unstable halides of N-phosphorylated imidazolium.[28] Triflate analogues of such salts appeared to be stable and were isolated. On treatment with strong bases the latter gave stable N-phosphorylated and N,N′-diphosphorylated imidazol-2-ylidenes, which were also isolated and characterized. The obtained imidazol-2-ylidenes rearranged to 2-phosphorylated imidazoles with heating.

Considering the probable generality of such a "carbene" mechanism for the rearrangement of N-phosphorylated 1,3-azoles, the investigation of intermediates of phosphorylation of 1,2,4-triazoles is of interest. Therefore, in continuing our studies on the mechanism of phosphorylation of nitrogen-containing heterocycles, we report here on the phosphorylation

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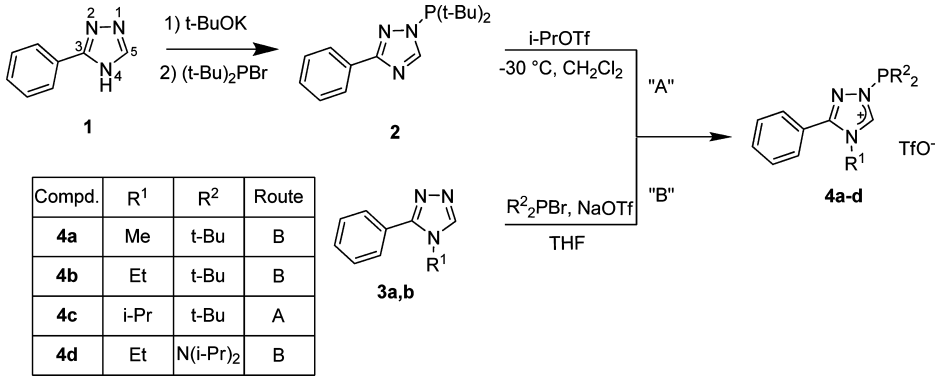
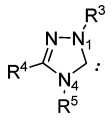
Scheme 1. Synthesis of Triazolium Salts 4a−d



Compd.	R^1	R^2	Route
4a	Me	t-Bu	B
4b	Et	t-Bu	B
4c	i-Pr	t-Bu	A
4d	Et	$N(i\text{-}Pr)_2$	B

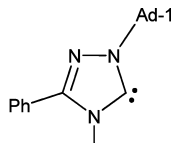
Table 1. Properties of Phosphorylated Triazol-5-ylidenes 5a−c and of Other Triazol-5-ylidenes 10−25 Reported in the Literature



10-25

substance no.	R^3	R^4	R^5	$\delta(^{13}C)$ C_5, ppm	$N_1-C_5-N_4$ angle, deg	bond length, Å: N_1-C_5	bond length, Å: N_4-C_5
5a	$P(t\text{-}Bu)_2$	Me	Ph	220.44			
5b	$P(t\text{-}Bu)_2$	Et	Ph	220.20			
5c	$P(t\text{-}Bu)_2$	i-Pr	Ph	220.57	102.12	1.350	1.359
10[3]	Ph	Ph	Ph	214.6	100.6	1.351	1.373
11[30]	t-Bu	4-F-C_6H_4−	Ph	206.6			
12[30]	t-Bu	4-F-C_6H_4−	2-Cl-C_6H_4−	208.6			
13[31]	1-Ad	4-R^6-C_6H_4−[a]	Ph	206.2	100.19	1.338	1.390
14[31]	1-Ad	3-R^6-C_6H_4−[a]	Ph	209.2			
15[32]	1-Ad	1-naphthyl	Ph	210.7			
16[32]	1-Ad	4-Br-C_6H_4-	Ph	210.6			
17[32]	1-Ad	Ph	Ph	212.7			
18[32]	1-Ad	4-Br-C_6H_4−	4-Br-C_6H_4−	210.1			
19[33]	Me	−CH═CHCH═CH−		203.8			
20[33]	Et	−CH═CHCH═CH−		203.8			
21[33]	Et	−CH═CHCH═CMe−		201.8			
22[33]	Ph	−CH═CHCH═CH−		204.2			
23[33]	Ph	−CH═CHCH═CMe−		204.7			
24[33]	2-(i-Pr)-C_6H_4−	−CH═CHCH═CH−		207.4			
25[33]	2-(i-Pr)-C_6H_4−	−CH═CHCH═CMe−		206.1			

[a] R^6 =



of 1,2,4-triazoles and on the synthesis of a new type of triazol-5-ylidene, **B** (Figure.1). Furthermore, we demonstrate here for the first time that N-phosphorylated azolylidene ligands can act as bidentate ligands toward metal centers, with NHC and trivalent phosphorus as coodination sites.

RESULTS AND DISCUSSION

The desired triazolium salts **4** were obtained by two routes (Scheme 1). The first includes transformation of 3-phenyl-4*H*-1,2,4-triazole (**1**) to potassium 3-phenyl-4*H*-1,2,4-triazolide, which is then phosphorylated by *t*-Bu_2PBr to form 1-(di-*tert*-butylphosphino)-3-phenyl-1*H*-1,2,4-triazole (**2**), a white crystalline compound that is sensitive to air. The ^{31}P NMR shift of triazole **2** at δ 98 ppm is in the usual range for phosphinous amides, although it lies downfield compared to that of the known 1-(diisopropylphosphino)-1*H*-1,2,4-triazole (δ 79 ppm).[29] Treatment of compound **2** with *i*-PrOTf in CH_2Cl_2 gives triazolium salt **4c**. In the ^{31}P NMR spectrum of the reaction mixture, two resonance signals appear (124 and 117 ppm, 1:1 ratio) which evidence that both N_2 and N_4 atoms are alkylated in the process. The N_2-alkylated isomer, characterized

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by a more upfield ^{31}P NMR shift, was not isolated. The target compound **4c** was separated by extraction with ether.

The second route (Scheme 1) involves phosphorylation of 4-alkyl-3-phenyl-4*H*-1,2,4-triazoles **3a,b** by *t*-Bu_2PBr/NaOTf or $(i\text{-}Pr_2N)_2POTf$ giving salts **4a,b,d**. As evidenced by the ^{31}P NMR spectra of reaction mixtures, phosphorylation occurs at either nitrogen atom—N_1 or N_2. Two resonance signals are observed (ca. 126 and 116 ppm (80:20) for **4a**, 128 and 114 ppm (85:15) for **4b**, only target compound for **4d**), with the peak representing the target compound lying downfield. Crystallization allows the separation and isolation of the target salts.

Compounds **4a−d** are light-colored, moisture-sensitive solids, exhibiting doublets of C_5 at δ ∼150−153 ppm with a coupling constant of ∼30 Hz in their ^{13}C NMR spectra. The peak of proton H_5 is, as expected, deshielded with a ^1H NMR shift of ∼10 ppm ($J \approx 3$ Hz).

Salts **4a−d** react with sodium bis(trimethylsilyl)amide in THF, forming N-phosphorylated triazolylidenes **5a−d**, which, except for **5d** (see below), could be isolated and characterized. They are air-sensitive, crystalline compounds, which do not show the H_5 signal at δ ∼10 ppm in the ^1H NMR spectra. In the ^{13}C NMR spectra, a highly deshielded signal, characteristic of a carbene center, emerges at δ ∼220 ppm. This peak appears in the range typical for nonphosphorylated (205−220 ppm) and N-phosphorylated (219−224 ppm)[28] imidazol-2-ylidenes. However, the carbene atoms of compounds **5a−c** have the most downfield shift among the known triazol-5-ylidenes (201−214 ppm) (cf. Table 1).

A single crystal of carbene **5c**, suitable for X-ray diffraction analysis, was grown from pentane. The X-ray crystal structure of compound **5c** is depicted in Figure 2. The $N_3-C_1-N_2$ angle

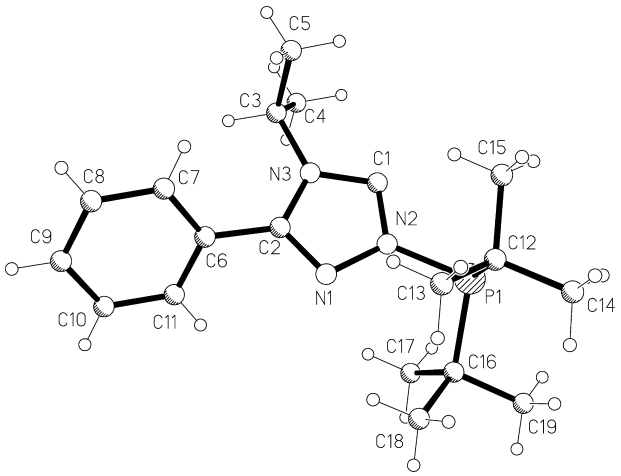

Figure 2. Molecular structure of **5c**. Selected bond lengths (Å) and angles (deg): C_1-N_3 = 1.359(4), N_3-C_2 = 1.384(4), C_2-N_1 = 1.303(4), N_1-N_2 = 1.416(3), N_2-C_1 = 1.350(4); $N_2-C_1-N_3$ = 102.1(2).

at the carbene center and the N_2-C_1 and N_3-C_1 bond lengths are in the range typical for NHCs (cf. Table 1). Planes of C_2-phenyl and triazole rings make up an angle of ca. 60°, twice as large as in the case of known triazol-5-ylidenes (ca. 30°).[3,31] Steric hindrance causes the isopropyl and di-*tert*-butylphosphino groups to twist out as well (corresponding torsion angles are $C_1-N_3-C_3-C_5$ = −74.5(4)° and $N_1-N_2-P_1-C_{12}$ = −73.7(2)°).

As is known, nonphosphorylated triazol-5-ylidenes often dimerize slowly at room temperature to give enetetramines.[33] However, such dimerization was not observed in the case of carbenes **5a−d** because of the availability of a more preferred path, namely rearrangement to 3-phosphorylated triazoles **6a−d** (Scheme 2). The thermal stability of carbenes **5a−d** toward such a rearrangement decreases in the sequence **5c** (R_1 = *i*-Pr, R_2 = *t*-Bu) > **5a** (R_1 = Me, R_2 = *t*-Bu) > **5b** (R_1 = Et, R_2 = *t*-Bu) > **5d** (R_1 = Et, R_2 = N(i-Pr)$_2$): for example, **5d** rearranges in a few hours at room temperature, which also accounts for the difficulty in its isolation, whereas the rearrangement of **5b** at the same temperature takes several days (see the Experimental Section for details). Furthermore, it is significant that N-phosphorylated triazol-5-ylidenes are less stable than the corresponding N-phosphorylated imidazol-2-ylidenes. Thus, heating to 90 °C for 50 min is required for the complete rearrangement **5a** → **6a**, whereas it takes 1 h at 150 °C for the rearrangement **26** → **27** (Scheme 3) to proceed to completion.[28]

It is important to remark that while it is well-known that phosphorylation of 1,2,4-triazoles in the presence of a base proceeds at the 3-position, no intermediates of this process have been ever isolated. In this work, N-phosphorylated 1,2,4-triazolium salts, N-phosphorylated triazolylidenes, and finally 3-phosphorylated triazoles were all isolated and characterized, and the interconversion between these species has been demonstrated. This leads us to postulate N-phosphorylated triazolylidenes as a likely intermediate in the phosphorylation process. Furthermore, experimental evidence suggests that such a carbene-mediated reaction of 1,2,4-triazoles with phosphorus(III) halides, and in particular the migration step of the phosphorus group from N to C, proceeds with an intermolecular reaction mechanism. We have in fact noted that a concentration increase leads to an increase in the rate of rearrangement. In addition, there is a well-studied migration of silyl groups from N to C in 1,2,4-triazoles which proved to be intermolecular in nature.[34] An intermolecular mechanism may also account for the observed difference in stability toward rearrengement of imidazol-5-ylidenes and 1,2,4-triazol-5-ylidenes: the former are more nucleophilic at carbon in comparison to the latter but presumably also less electrophilic at phosphorus; hence, the sum of these factors may result in higher stability of N-phosphorylated imidazol-5-ylidenes.

3-Phosphorylated triazoles **6a−d** were transformed into selenium derivatives **7a−d** (Scheme 2). On the other hand, as in the case of most NHCs, compounds **5a−d** add first selenium to divalent carbon, forming selones **8a−d**; subsequent oxidation of phosphorus atom with Se takes place only under prolonged (15−120 h) treatment of selones **8a−d** with Se (Scheme 2).[28]

The structure of compounds **5a−d**, exhibiting two strongly σ-donating but chemically different coordinating groups at the carbene carbon and at the trivalent phosphorus atom, makes them very interesting bidentate ligands for transition metals. Although coordination of these ligands in a chelating fashion is not in principle precluded, the formation of a four-membered ring obviously disfavors this coordination mode; consequently, it is expected that such compounds should preferably act as bridging ligands between two metal centers. Indeed, air-stable silver(I) complexes **28b,c** were obtained by reaction of silver oxide with 2 equiv of **4b,c**, respectively, in dichloromethane (Scheme 4). After workup, complexes **28b,c** were isolated as highly thermally stable white crystals.

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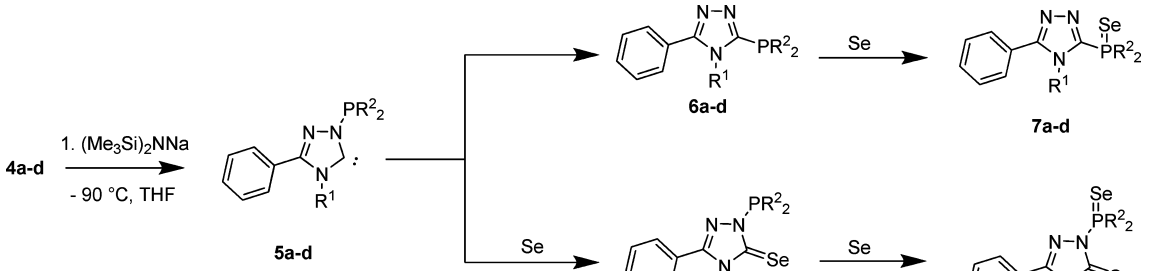
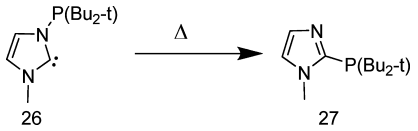
Scheme 2. Chemical Properties of Carbenes 5

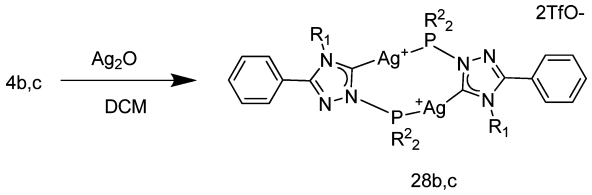


Compd.	R^1	R^2
a	Me	t-Bu
b	Et	t-Bu
c	i-Pr	t-Bu
d	Et	$N(i\text{-}Pr)_2$

Scheme 3. Rearrangement of Imidazol-2-ylidene 26



Scheme 4. Synthesis of Silver Complexes 28



The molecular structure of **28b** was determined by means of single-crystal X-ray diffraction analysis (Figure 3). As expected, the complex is dinuclear, with C–Ag–P angles of ca. 168°. Ag–C and Ag–P bond lengths (Ag–C = 2.12 Å, Ag–P = 2.37 Å) are in agreement with those of other silver(I) carbene and phosphine complexes previously reported.[33,35] The Ag–Ag distance (2.881 Å) is small and comparable to the conventionally tabulated covalent radius for silver (1.45 ± 0.05 Å), although estimates of this parameter in the case of two-coordinate silver(I) compounds point instead to a value of 1.33 Å.[36] A covalent bond formation cannot be postulated between the two silver(I) centers, but it is likely that closed-shell d^{10}–d^{10} interactions are present at such a short intermetallic distance.[37] Triazole rings are planar; moreover, silver atoms and adjacent phosphorus atoms all lie in the same plane. In comparison to a related parent carbene (Table 2) the geometry of the triazole ring is not subject to substantial changes, except for some shortening of bond distances (ca. 0.01 Å).

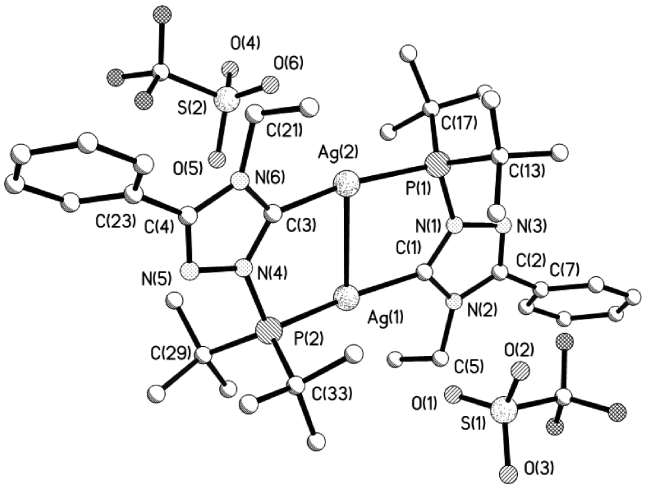


Figure 3. Molecular structure of **28b**. Selected bond lengths (Å) and angles (deg): C_1–N_2 = 1.35(1), N_2–C_2 = 1.377(8), C_2–N_3 = 1.29(1), N_3–N_1 = 1.410(9), N_1–C_1 = 1.335(9), P_1–Ag_2 = 2.398(2), C_1–Ag_1 = 2.146(6); N_2–C_1–N_1 = 103.2(6), C_1–Ag_1–P_2 = 166.9(2).

Table 2. Comparison of the Properties of Triazol-5-ylidene 5c and Complex 28b

substance no.	R^3	R^4	R^5	$\delta(^{13}C)$ C_5, ppm	N_1–C_5–N_4 angle, deg	bond length, Å: N_1–C_5	bond length, Å: N_4–C_5
5c	P(t-Bu)$_2$	i-Pr	Ph	220.57	102.12	1.350	1.359
28b	P(t-Bu)$_2$	Et	Ph	174.10	103.23	1.335	1.353

In conclusion, synthetic routes to N-phosphorylated triazolium triflates were developed. It was shown that the obtained triazolium salts react with strong bases to form N-phosphorylated triazol-5-ylidenes, which rearrange to C-phosphorylated triazoles with heating. Triazolium salts react with silver(I) oxide to give novel and highly stable dinuclear phosphinocarbene complexes. Further investigations on the properties of these complexes as well as on their use as transmetalating reagents toward other metal centers are currently underway.

EXPERIMENTAL SECTION

General Methods. All procedures with air- and moisture-sensitive compounds were performed under an atmosphere of dry argon in flame-dried glassware. Compounds **1** and **3** were dried before use by distillation in vacuo over P_2O_5. Solvents were purified and dried by standard methods. Melting points were determined with an electrothermal capillary melting point apparatus and were uncorrected. ^{1}H NMR spectra were recorded on spectrometers working at 500.13 or

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299.94 MHz. ^{13}C NMR spectra were recorded at 125.75 MHz. ^{31}P NMR spectra were recorded at 121.42 MHz. Chemical shifts (δ) are reported in ppm downfield relative to internal TMS (for ^{1}H, ^{13}C) and external 85% H_3PO_4 (for ^{31}P). Chromatography was performed on silica gel 60 (0.040−0.063 mm).

Crystallographic measurements were performed at 173(1) K on a diffractometer operating in the ω and φ scan modes. The structure was solved by direct methods refined by full-matrix least-squares techniques in anisotropic approximation for non-hydrogen atoms using SHELXS97 and SHELXL97 program packages. Hydrogen atoms were located from Fourier synthesis and refined isotropically.

3-(Di-*tert*-butylphosphino)-5-phenyl-4*H*-1,2,4-triazole (2). Solution of **1** (3.36 g, 23.1 mmol) in THF (20 mL) was added to cooled solution of *t*-BuOK (3.10 g, 27.6 mmol) in THF (25 mL). The precipitate that formed was filtered. Yield: 3.98 g (94%). A solution of *t*-Bu_2PBr (4.55 g, 20.2 mmol) in THF (17 mL) was added to a frozen suspension of potassium 3-phenyl-1,2,4-triazolide (3.70 g, 20.2 mmol) in THF (34 mL). The mixture was warmed to room temperature, filtered from KBr precipitate, and evaporated. The obtained residue was crystallized from pentane. Yield: 5.18 g (89%) of a light yellow powder. Mp: 52−53 °C. Bp: 140−145 °C/0.05 mm. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.27 (d, J = 13 Hz, 18 H), 7.41 (br d, J = 7.5 Hz, 1H), 7.45 (br t, J = 7, 2H), 8.20 (d, J = 8, 2H), 8.34 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.81 (d, J = 15.1 Hz), 35.12 (d, J = 22.6 Hz), 126.56, 128.54, 129.26, 131.24, 153.60 (d, J = 3.6 Hz), 164.84. ^{31}P NMR (81 MHz, $CDCl_3$): δ 98.0. Anal. Calcd for $C_{16}H_{24}N_3P$ (289.36): C, 66.41; H, 8.36; N, 14.52. Found: C, 66.30; H, 8.49; N, 14.33.

1-(Di-*tert*-butylphosphino)-4-methyl-3-phenyl-4*H*-1,2,4-triazol-1-ium Trifluoromethanesulfonate (4a). *t*-Bu_2PBr (5.44 g, 24.2 mmol) was added to a solution of **3a** (3.40 g, 21.3 mmol) and sodium trifluoromethanesulfonate (7.17 g, 41.7 mmol) in THF (24 mL). The resulting solution was stirred for 20 h at room temperature. Then solvent was removed in vacuo, and the residue was washed with ether and crystallized from CH_2Cl_2. Yield: 5.75 g (59%) of white crystals. Mp: 108−111 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.30 (d, J = 13.5 Hz, 18H), 4.15 (s, 3H), 7.52−7.76 (br m, 5H), 10.12 (d, J = 2.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.46 (d, J = 16.3 Hz), 35.25, 35.88 (d, J = 28.9 Hz), 122.40, 123.23 (q, J = 334,4 Hz), 128.93, 129.30, 129.53, 152.69 (d, J = 30.2 Hz), 156.70. ^{31}P NMR (81 MHz, $CDCl_3$): δ 126.8. ^{19}F NMR (188 MHz, $CDCl_3$): δ −79.0. Anal. Calcd for $C_{18}H_{27}F_3N_3O_3PS$ (453.46): C, 47.68; H, 6.00; N, 9.27. Found: C, 47.54; H, 6.17; N, 9.43.

1-(Di-*tert*-butylphosphino)-4-ethyl-3-phenyl-4*H*-1,2,4-triazol-1-ium Trifluoromethanesulfonate (4b). *t*-Bu_2PBr (7.42 g, 33 mmol) was added to a solution of **3b** (5.71 g, 33.0 mmol) and sodium trifluoromethanesulfonate (5.67 g, 33.0 mmol) in THF (28 mL). The resulting solution was stirred for 4 days at 16 °C. Then solvent was removed in vacuo and the residue was extracted with CH_2Cl_2. The solvent was evaporated, and the residue obtained after extraction was carefully washed with ether and benzene (34 mL). Crystals were filtered and dried in vacuo. Yield: 9.75 g (63%) of colorless crystals. Mp: 121−123 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.33 (d, J = 13.5 Hz, 18H), 1.52 (t, J = 7.5 Hz, 3H), 4.60 (q, J = 7.5 Hz, 2H), 7.61−7.73 (br m, 5H), 10.23 (d, J = 3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.90, 28.46 (d, J = 16.3 Hz), 35.90 (d, J = 28.8 Hz), 44.01, 120.67 (q, J = 319.4 Hz), 122.64, 129.16, 129.64, 132.54, 151.67 (d, J = 30 Hz), 156.30 (d, J = 2.5 Hz). ^{31}P NMR (81 MHz, $CDCl_3$): δ 128.6. ^{19}F NMR (188 MHz, $CDCl_3$): δ −78.6. Anal. Calcd for $C_{19}H_{29}F_3N_3O_3PS$ (467.49): C, 48.81; H, 6.25; N, 8.99. Found: C, 48.72; H, 6.11; N, 8.73.

1-(Di-*tert*-butylphosphino)-4-isopropyl-3-phenyl-4*H*-1,2,4-triazol-1-ium Trifluoromethanesulfonate (4c). A solution of isopropyl trifluoromethanesulfonate (2.04 g, 10.6 mmol) in CH_2Cl_2 (8 mL) was added to a frozen solution of **2** (3.07 g, 10.6 mmol) in CH_2Cl_2 (15 mL). After a day at room temperature the solvent was evaporated and the residue was extracted with warm ether. Yield: 1.68 g (33%) of light yellow crystals. Mp: 112−114 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.35 (d, J = 13 Hz, 18 H) 1.67 (d, J = 7 Hz, 6H), 4.82 (m, 1H), 7.6−7.7 (br m, 5H), 10.37 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.64, 28.46 (d, J = 16.3 Hz,), 35.93 (d, J = 30.2 Hz), 52.92, 129.35, 129.76, 132.58, 120.72 (q, J = 320.5 Hz), 122.77, 150.30 (d, J = 31.4 Hz), 156.12 (d, J = 2.5 Hz). ^{31}P NMR (81 MHz, $CDCl_3$): δ 127.4. ^{19}F NMR (188 MHz, $CDCl_3$): δ −79.9. Anal. Calcd for $C_{20}H_{31}F_3N_3O_3PS$ (481.51): C, 49.89; H, 6.49; N, 8.73. Found: C, 49.67; H, 6.31; N, 8.55.

1-[Bis(diisopropylamino)phosphino]-4-ethyl-3-phenyl-4*H*-1,2,4-triazol-1-ium Trifluoromethanesulfonate (4d). A solution of **3b** (1.33 g, 7.7 mmol) in CH_2Cl_2 (7.5 mL) was added to a solution of bis(diisopropylamino)phosphonium trifluoromethanesulfonate (2.8 g, 7.3 mmol) in CH_2Cl_2 (7.5 mL) cooled to −30 °C. The solution was warmed to room temperature, and solvent was evaporated. The obtained residue was dissolved in Et_2O at 40 °C and was cooled to −15 °C for crystallization. The crystals that formed were washed with cool ether and dried in vacuo. Yield: 3.80 g (94%) of a light yellow powder. Mp: 103−105 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.19 (d, J = 6.9 Hz, 24H), 1.42 (t, J = 7.2 Hz, 3H), 3.67 (sept, J = 6.6 Hz, 4H), 4.43 (q, J = 7.2 Hz, 2H), 7.6 (m, 5H), 9.57 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.69, 23.64 (d, J = 8.8 Hz), 43.00, 48.26 (d, J = 12.6 Hz), 120.76 (q, J = 320.6 Hz), 123.28, 129.01, 129.60, 132.10, 144.76, 154.57. ^{31}P NMR (81 MHz, $CDCl_3$): δ 120.7. ^{19}F NMR (188 MHz, $CDCl_3$): δ −78.5. Anal. Calcd for $C_{23}H_{39}F_3N_5O_3PS$ (553.62): C, 49.90; H, 7.10; N, 12.65. Found: C, 49.73; H, 7.01; N, 12.43.

1-(Di-*tert*-butylphosphino)-4-methyl-3-phenyl-1,2,4-triazol-5-ylidene (5a). Compound **4a** (2.87 g, 6.30 mmol) was dissolved in THF (11 mL) and cooled to −95 °C. Then a solution of NaHMDS (1.16 g, 6.30 mmol) in THF (11 mL) was added over 10 min. The mixture was warmed to room temperature, and ^{31}P NMR was unchanged throughout this time. Solvent was removed in vacuo, the residue obtained was extracted with pentane (40 mL), and the extract was held at −6 °C for 3 days for crystallization of the product. The remainder from extraction was extracted with CH_2Cl_2 for isolation of additional quantities of product. The crystals obtained were joined. Overall yield: 1.34 g (70%) of yellow crystals. Mp: 101−103 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 1.34 (d, J = 12 Hz, 18H), 3.49 (s, 3H), 7.0 (m, 3H), 7.34 (d, J = 7 Hz, 2H). ^{13}C NMR (125 MHz, C_6D_6): δ 28.82 (d, J = 16.3 Hz), 34.60 (d, J = 26.4 Hz), 34.91, 127.1, 128.41, 128.69, 129.47, 153.39, 220.44 (d, J = 62.9 Hz). ^{31}P NMR (81 MHz, C_6D_6): δ 101.1. Anal. Calcd for $C_{17}H_{26}N_3P$ (303.38): C, 67.30; H, 8.64; N, 13.85. Found: C, 67.19; H, 8.45; N, 13.71.

1-(Di-*tert*-butylphosphino)-4-ethyl-3-phenyl-1*H*-1,2,4-triazolyl-5-ylidene (5b). A solution of NaHMDS (0.79 g, 4.3 mmol) in THF (9 mL) was added to a −90 °C solution of **4b** (2.02 g, 4.30 mmol) in THF (14 mL) over 5 min. The reaction mixture was held for 15 min at 100 °C. Then the solvent was thoroughly evaporated in vacuo and the residue that was obtained was extracted with pentane (56 mL). The crude product was crystallized from pentane. Yield: 0.47 g (34%) of white crystals. Mp: 75−76 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 1.21 (br t, 3H), 1.37 (d, J = 12.3 Hz, 18 H), 3.96 (q, J = 6.9 Hz, 3H), 7.02−7.10 (br m, 3H), 7.30−7.36 (br m, 2H). ^{13}C NMR (125 MHz, C_6D_6): δ 16.60, 28.85 (d, J = 15.1 Hz), 34.64 (d, J = 27.7 Hz), 42.32, 122.16, 128.49, 128.75, 129.46, 152.99, 220.20 (d, J = 62.9 Hz). ^{31}P NMR (81 MHz, C_6D_6): δ 103.2. Anal. Calcd for $C_{18}H_{28}N_3P$ (317.40): C, 68.11; H, 8.89; N, 13.24. Found: C, 68.33; H, 8.95; N, 13.39.

1-(Di-*tert*-butylphosphino)-4-isopropyl-3-phenyl-1*H*-1,2,4-triazolyl-5-ylidene (5c). A solution of NaHMDS (0.61 g, 3.3 mmol) in THF (11 mL) was added at −95 °C over 10 min to a solution of **4c** (1.6 g, 3.3 mmol) in THF (11 mL). The mixture was warmed to room temperature, and the solvent was evaporated in vacuo. The residue was twice crystallized from degassed pentane (37 mL for the first time, 11 mL for the second). Yield: 0.35 g (32%) of a white powder. Mp: 91−92 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 0.84 (m, 1H), 0.99 (d, J = 17 Hz, 6H), 1.34 (d, J = 12 Hz, 18 H), 7.5 (br m, 4H), 7.27 (t, J = 8 Hz, 1H). ^{13}C NMR (125 MHz, C_6D_6): δ 26.00, 28.94 (d, J = 16.3 Hz), 34.68 (d, J = 27.7 Hz), 48.41, 128.56, 129.09, 129.45, 140.76, 152.59, 220.57 (d, J = 62.9 Hz). ^{31}P NMR (81 MHz, C_6D_6): δ 101.0. Anal. Calcd for $C_{19}H_{30}N_3P$ (331.43): C, 68.85; H, 9.12; N, 12.68. Found: C, 68.72; H, 9.33; N, 12.79.

3-(Di-*tert*-butylphosphino)-4-methyl-5-phenyl-4*H*-1,2,4-triazole (6a). Compound **5a** (0.1 g., 0.3 mmol) was dissolved in benzene

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(0.6 mL), and the solution was heated to 90 °C for 50 min. The solvent was evaporated. and the residue was crystallized from pentane. Quantitative yield (0.1 g) of light yellow crystals. Mp: 142−143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (d, J = 12.8 Hz, 18H), 3.79 (s, 3H), 7.53−7.62 (br m, 5H). ^{13}C NMR δ 29.01 (d, J = 17.6 Hz), 35.44, 36.36 (d, J = 28.9 Hz), 125.78, 128.57, 129.16, 131.12, 153.60, 173.15 (d, J = 30.2 Hz). ^{31}P NMR (81 MHz, $CDCl_3$): δ 97.5. Anal. Calcd for $C_{17}H_{26}N_3P$ (303.38): C, 67.30; H, 8.64; N, 13.85. Found: C, 67.51; H, 8.45; N, 13.91.

3-(Di-*tert*-butylphosphino)-4-ethyl-5-phenyl-4*H*-1,2,4-triazole (6b). A solution of **5b** (0.1 g in 0.5 mL of C_6D_6) was held for 4 days at 25 °C Then benzene was evaporated, and the residue was crystallized from pentane (1.6 mL). Yield: 0.06 g (60%) of a white powder. Mp: 94−97 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 1.20−1.32 (br m, 21H), 3.96 (m, 2H), 7.11−7.19 (m, 3H), 7.56 (m, 2H). ^{13}C NMR (125 MHz, C_6D_6): δ 15.99, 22.34, 30.05 (d, J = 13.8 Hz), 33.22 (d, J = 15.1 Hz), 39.20 (d, J = 15.1 Hz), 128.54, 128.69, 129.20, 129.01, 154.33 (d, J = 1.2 Hz). ^{31}P NMR (81 MHz, C_6D_6): δ 3.7. Anal. Calcd for $C_{18}H_{28}N_3P$ (317.41): C, 68.11; H, 8.89; N, 13.24. Found: C, 68.17; H, 8.76; N, 13.33.

3-(Di-*tert*-butylphosphino)-4-isopropyl-5-phenyl-4*H*-1,2,4-triazole (6c). Carbene **5c** (0.1 g, 0.3 mmol) was dissolved in benzene (0.5 mL). The solution was heated for 1 h at 90 °C. Then the solvent was evaporated and the residue was crystallized from pentane (1.6 mL). Yield: 0.09 g (90%) of a light yellow powder. Mp: 103−104 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.19 (d, J = 6.5 Hz, 6H), 1.36 (d, J = 17.5 Hz, 18H), 4.04 (sept., J = 6.5 Hz, 1H), 7.31 (m, 3H), 7.56 (d, J = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.60, 26.19, 38.60 (d, J = 73.8 Hz), 48.52, 114.58 (d, J = 1.2 Hz), 127.87, 127.99, 128.57, 140.06 (d, J = 2.5 Hz), 156.42 (d, J = 8.8 Hz). ^{31}P NMR (81 MHz, $CDCl_3$): δ 13.3 (m). Anal. Calcd for $C_{19}H_{30}N_3P$ (331.44): C, 68.85; H, 9.12; N, 12.68. Found: C, 68.69; H, 9.21; N, 12.73.

3-[Bis(diisopropylamino)phosphino]-4-ethyl-5-phenyl-4*H*-1,2,4-triazole (6d). A solution of NaHMDS (0.51 g, 2.8 mmol) in THF (11 mL) was added over 10 min to a −90 °C solution of **4d** (1.53 g, 2.8 mmol) in THF (11 mL). The mixture was warmed to room temperature and was held for 5 h. Then the solvent was evaporated and the residue was crystallized from pentane. Yield: 0.98 g (88%), colorless crystals. Mp: 126−127 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.12 (d, J = 6.5 Hz, 12H), 1.28 (d, J = 6.5 Hz, 12H), 1.31 (t, J = 7 Hz, 3H), 3.73 (sept, J = 6.5 Hz, 4H), 4.16 (q. d, J = 7 Hz, J = 2 Hz, 2H), 7.4 (m, 3H), 7.6 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.15 (d, J = 5.0 Hz), 23.70 (d, J = 7.5 Hz), 23.90 (d, J = 5.0 Hz), 39.33 (d, J = 12.6 Hz), 48.18 (d, J = 11.3 Hz), 128.47, 128.70, 128.74, 129.47, 153.84 (d, J = 2.5 Hz), 158.04 (d, J = 13.8 Hz); ^{31}P NMR (81 MHz, $CDCl_3$): δ 25.3. Anal. Calcd for $C_{22}H_{38}N_5P$ (403.54): C, 65.48; H, 9.49; N, 17.35. Found: C, 65.61; H, 9.63; N, 17.44.

3-(Di-*tert*-butylphosphoroselenoyl)-4-methyl-5-phenyl-4*H*-1,2,4-triazole (7a). Compound **6a** (0.1 g., 0.3 mmol) was dissolved in benzene (1 mL), and Se (0.05 g, 0.63 mmol) was added. The mixture was stirred for 20 h at 15 °C. Then the solvent was evaporated and the residue was crystallized from pentane. The product was purified by plate chromatography on SiO_2, eluent CH_2Cl_2. The fraction with R_f = 0.5−0.7 was separated. Yield: 0.09 g (90%). Mp: 113−114 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.53 (d, J = 17.0 Hz, 18H), 4.25 (s, 3H), 7.55 (br m, 3H), 7.66 (br m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 27.97 (d, J = 2.5 Hz), 35.96, 40.76 (d, J = 33.9 Hz), 1256.66, 128.91, 129.43, 130.41, 157.44 (d, J = 5.0 Hz), 143.14 (d, J = 70.4 Hz). ^{31}P NMR (81 MHz, $CDCl_3$): δ 63.1.MS m/z (EI): 160.1, 328.0, 382.0, 384.1, 387.1. Anal. Calcd for $C_{17}H_{26}N_3PSe$ (382.34): C, 53.40; H, 6.85; N, 10.99. Found: C, 53.51; H, 6.71; N, 10.82.

3-(Di-*tert*-butylphosphoroselenoyl)-4-ethyl-5-phenyl-4*H*-1,2,4-triazole (7b). Compound **6b** (0.06 g., 0.19 mmol) was dissolved in benzene (2 mL), and Se (0.015 g, 0.18 mmol) was added. The mixture was stirred for 15 h at 15 °C. Then the mixture was filtered off, the filtrate was evaporated, and the residue was purified by plate chromatography on SiO_2, eluent CH_2Cl_2. The fraction with R_f = 0.05−0.15 was separated and crystallized from pentane. Yield: 0.06 g (80%) of pale crystals. Mp: 112−113 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23 (t, J = 6.9 Hz, 3H), 1.49 (d, J = 17.1 Hz, 18H), 4.91 (q, J = 6.9 Hz, 2H), 7.49−7.61 (br m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.32, 27.97 (d, J = 1.2 Hz), 40.74 (d, J = 40.0 Hz), 41.18, 127.34, 128.94, 129.22, 130.34, 142.22 (d, J = 125.7 Hz), 156.92 (d, J = 5.0 Hz). ^{31}P NMR (81 MHz, $CDCl_3$): δ 64.0. Anal. Calcd for $C_{18}H_{28}N_3PSe$ (396.37): C, 54.54; H, 7.12; N, 10.60. Found: C, 54.47; H, 7.25; N, 10.41.

3-(Di-*tert*-butylphosphoroselenoyl)-4-isopropyl-5-phenyl-4*H*-1,2,4-triazole (7c). Compound **6c** (0.090 g., 0.27 mmol) was dissolved in benzene (1 mL), and Se (0.050 g,6.3 mmol) was added. The mixture was stirred for 20 h at 15 °C. Then the solvent was evaporated and the residue obtained was purified by plate chromatography on SiO_2, eluent CH_2Cl_2. The fraction with R_f = 0.3−0.4 was isolated. Yield: 0.10 g (95%) of a light yellow powder. Mp: 180−182 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (d, J = 16.4 Hz, 18 H) 1.39 (d, J = 6.4 Hz, 6H), 4.56 (br s, 1H), 7.25 (t, J = 3.6 Hz, 2H), 7.42 (t, J = 7.8 Hz, 2H), 7.50 (br t, J = 8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.59, 27.84, 40.32 (d, J = 52.8 Hz), 48.67, 108.24, 127.96, 128.28, 129.16, 130.93, 164.01. ^{31}P NMR (81 MHz, $CDCl_3$): δ 88.8. MS m/z (EI): 241.0, 309.0, 409.2, 410.2, 412.2. Anal. Calcd for $C_{19}H_{30}N_3PSe$ (410.39): C, 55.61; H, 7.37; N, 10.24. Found: C, 55.48; H, 7.51; N, 10.43.

3-[Bis(diisopropylamino)phosphoroselenoyl]-4-ethyl-5-phenyl-4*H*-1,2,4-triazole (7d). Compound **6d** (0.35 g, 0.87 mmol) was dissolved in benzene (3.5 mL), and Se (0.30 g, 3.8 mmol) was added. The mixture was stirred for 20 h at 19 °C. Then the precipitate was filtered off and the filtrate was evaporated. The residue obtained was purified by plate chromatography on SiO_2, eluent CH_2Cl_2. The fraction with R_f = 0.1−0.35 was separated and crystallized from pentane. Yield: 0.21 g (50%) of a white powder. Mp: 147−148 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23 (t, J = 7.3 Hz, 3H), 1.34 (d, J = 7.0 Hz, 12H), 1.44 (d, J = 7.0 Hz, 12H), 4.14 (sept, J = 6.8 Hz, 4H), 4.75 (q, J = 6.9 Hz, 2H), 7.5 (m, 3H), 7.6 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.73, 23.86 (d, J = 3.8 Hz), 23.97 (d, J = 2.5 Hz), 41.13, 48.62 (d, J = 6.3 Hz), 127.93, 128.86, 128.90, 130.11, 149.93 (d, J = 145.8 Hz), 156.76 (d, J = 7.5 Hz). ^{31}P NMR (81 MHz, $CDCl_3$): δ 44.8. MS m/z (EI): 174.2, 383.2, 440.2, 482.2, 484.2, 487.2. Anal. Calcd for $C_{22}H_{38}N_5PSe$ (482.50): C, 54.76; H, 7.94; N, 14.51. Found: C, 54.61; H, 7.81; N, 14.37.

2-(Di-*tert*-butylphosphino)-4-methyl-5-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-selone (8a). Selenium (0.28 g, 3.5 mmol) was added to a solution of **5a** (1.1 g, 3.6 mmol) in benzene (6 mL). The mixture was held for 1 h at room temperature, the solvent was removed in vacuo, and the residue obtained was extracted with pentane (3 × 20 mL). Pentane was evaporated. Yield: 0.80 g (58%) of colorless crystals. Mp: 153−154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (d, J = 12.8 Hz, 18H), 3.79 (s, 3H), 7.52−7.61 (br m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 29.01 (d, J = 17.6 Hz), 35.44, 36.36 (d, J = 28.9 Hz, 125.78, 128.57, 129.16, 131.12, 153.60 (d, J = 1.3 Hz), 173.15 (d, J = 30.2 Hz). ^{31}P NMR (81 MHz, $CDCl_3$) 97.5. Anal. Calcd for $C_{17}H_{26}N_3PSe$ (382.34): C, 53.40; H, 6.85; N, 10.99. Found: C, 53.51; H, 6.73; N, 10.79.

2-(Di-*tert*-butylphosphino)-4-ethyl-5-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-selone (8b). Selenium (0.20 g, 2.5 mmol) was added to a solution of **5b** (0.79 g., 2.5 mmol) in benzene (6 mL). The mixture was held for 2 h at 0 °C. Solvent was evaporated; the residue obtained was extracted with pentane (2 × 32 mL) and crystallized from pentane (16 mL). Yield: 0.56 g (57%) of light yellow crystals. Mp: 164−165 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.3 (br m, 21H), 4.34 (quad, J = 7.2 Hz, 2H), 7.58 (br m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.05, 28.99 (d, J = 17.6 Hz), 36.32 (d, J = 28.9 Hz), 42.68, 125.97, 128.49, 129.20, 131.07, 153.48, 172.21 (d, J = 30.2 Hz). ^{31}P NMR (81 MHz, $CDCl_3$): δ 99.08. Anal. Calcd for $C_{18}H_{28}N_3PSe$ (396.37): C, 54.54; H, 7.12; N, 10.60. Found: C, 54.31; H, 7.01; N, 10.45.

2-(Di-*tert*-butylphosphino)-4-isopropyl-5-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-selone (8c). Se (0.18 g, 2.2 mmol) was added to a solution of **5c** (0.75 g, 2.3 mmol) in benzene (6 mL). The suspension was stirred for 2 h at 15 °C, and then solvent was evaporated. The residue was extracted with pentane (3 × 20 mL). Yield: 0.68 g (75%) of a white powder. Mp: 130−131 °C. ^{1}H NMR

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(500 MHz, $CDCl_3$): δ 1.27 (d, J = 12.5 Hz, 18H), 1.40 (d, J = 6 Hz, 6H), 5.26 (br s, 1H), 7.44 (d, J = 6.5 Hz, 2H), 7.51 (t, J = 7.5 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.96, 29.02 (d, J = 16.3 Hz), 36.36 (d, J = 28.9 Hz), 52.49, 127.37, 128.72, 129.74, 130.83, 153.77, 171.54 (d, J = 31.4 Hz). ^{31}P NMR (81 MHz, $CDCl_3$): δ 96.0. Anal. Calcd for $C_{19}H_{30}N_3PSe$ (410.39): C, 55.61; H, 7.37; N, 10.24. Found: C, 55.43; H, 7.23; N, 10.11.

2-[Bis(diisopropylamino)phosphino]-4-ethyl-5-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-selone (8d). A solution of NaHMDS (0.78 g, 4.2 mmol) in THF (5.6 mL) was added over 10 min to a −90 °C solution of **4d** (2.36 g, 4.26 mmol) in THF (9 mL). After 30 min of stirring at −90 °C Se (0.34 g, 4.3 mmol) was added. The mixture was warmed to 0 °C and was held for 15 h. The solvent was evaporated, and the residue was extracted with pentane (3 × 10 g) and crystallized from 5 g of pentane. Yield: 1.8 g (90%) of a light yellow powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.18 (d, J = 6.9 Hz, 12H), 1.24 (d, J = 6.9 Hz, 12H), 1.28 (t, J = 7.2 Hz, 3H), 3.64 (sept., J = 6.5 Hz, 4H), 4.25 (q, J = 7.2 Hz, 2H), 7.5 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.30, 23.56 (d, J = 8.8 Hz), 24.10 (d, J = 6.3 Hz), 41.26, 47.19 (d, J = 13.8 Hz), 126.85, 128.46, 129.12, 130.62, 152.44 (d, J = 1.2 Hz), 162.43 (d, J = 30.2 Hz). ^{31}P NMR (81 MHz, $CDCl_3$): δ 97.0. Anal. Calcd for $C_{22}H_{38}N_5PSe$ (482.50): C, 54.76; H, 7.94; N, 14.51. Found: C, 54.59; H, 7.73; N, 14.38.

2-(Di-*tert*-butylphosphoroselenoyl)-4-methyl-5-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-selone (9a). Compound **8a** (0.58 g, 1.5 mmol) was dissolved in pyridine (2 mL), and Se (0.30 g, 3.8 mmol) was added. The mixture was stirred for 1 day at room temperature. Pyridine was evaporated, and the residue was extracted with benzene. Benzene was evaporated, and the residue was purified by plate chromatography on SiO_2, eluent CH_2Cl_2. The fraction with R_f = 0.3−0.5 was separated. Yield: 0.45 g (64%) of pale crystals. Mp: 158−159 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.55 (d, J = 17.5 Hz, 18H), 3.71 (s, 3H), 7.57 (s, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 28.76, 34.56, 45.07 (d, J = 35.2 Hz), 125.03, 128.71, 129.37, 131.58, 152.12 (d, J = 5.0 Hz), 170.47 (d, J = 7.5 Hz). ^{31}P NMR (81 MHz, $CDCl_3$): δ 120.3. MS m/z (EI): 160.0, 237.8, 380.0, 456.0, 461.0, 462.0, 464.0. Anal. Calcd for $C_{17}H_{26}N_3PSe_2$ (461.30): C, 44.26; H, 5.68; N, 9.11. Found: C, 44.42; H, 5.81; N 9.32.

2-(Di-*tert*-butylphosphoroselenoyl)-4-ethyl-5-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-selone (9b). Compound **8b** (0.2 g, 0.5 mmol) was dissolved in benzene (2.3 mL), and Se (0.06 g, 0.76 mmol) was added. The mixture was stirred for 4 days at 16 °C. Then the solvent was evaporated and the residue was purified by plate chromatography on SiO_2. The fraction with R_f = 0.2−0.6 was separated and crystallized from hexane. Yield: 0.17 g (72%) of white crystals. Mp: 193−195 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (t, J = 7.3 Hz, 3H), 1.57 (d, J = 18 Hz, 18H), 4.27 (quad, J = 6.9 Hz, 2H), 7.51 (br m, 3H), 7.65 (br m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 15.52, 28.53 (d, J = 2.5 Hz), 41.13, 44.78 (d, J = 21.4 Hz), 127.90, 128.79, 128.82, 130.07, 140.38 (d, J = 6.3 Hz), 156.45. ^{31}P NMR (81 MHz, $CDCl_3$): δ 125.0 (m). MS m/z (EI): 174.0, 249.8, 470.0, 475.0, 476.0. Anal. Calcd for $C_{18}H_{28}N_3PSe_2$ (475.33): C, 45.48; H, 5.94; N, 8.84. Found: C, 45.65; H, 5.73; N, 8.67.

2-(Di-*tert*-butylphosphoroselenoyl)-4-isopropyl-5-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-selone (9c). Se (0.1 g, 1.3 mmol) was added to 0.23 g (0.56 mmol) of **8c**, dissolved in pyridine (2 mL). The mixture was held for 15 h at 15 °C. The solution obtained was partitioned by plate chromatography on SiO_2, eluent CH_2Cl_2. The fraction with R_f = 0.2−0.4 was isolated. Yield: 0.2 g (73%) of a colorless powder. Mp: 148−149 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.31 (s, 6H), 1.55 (d, J = 17.5 Hz, 18 H), 5.59 (s, 1H), 7.44 (d, J = 8 Hz, 2H), 7.55 (t, J = 7.5 Hz, 2H), 7.61 (t, J = 7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.06, 28.84, 45.25 (d, J = 35.2 Hz), 51.14, 127.01, 128.82, 129.72, 131.14, 152.06 (d, J = 6.3 Hz), 169.71. ^{31}P NMR (81 MHz, $CDCl_3$): δ 120.2. Anal. Calcd for $C_{19}H_{30}N_3PSe_2$ (489.35): C, 46.63; H, 6.18; N, 8.59. Found: C, 46.48; H, 6.32; N, 8.41.

2-[Bis(diisopropylamino)phosphoroselenoyl]-4-ethyl-5-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-selone (9d). A solution of NaHMDS (0.71 g, 3.9 mmol) in THF (11 mL) was added over 10 min to a −90 °C solution of **4d** (2.2 g, 3.9 mmol) in THF (11 mL). The mixture was stirred for 20 min at −85 °C. Then Se (0.86 g, 11 mmol) was added and the reaction mixture was stirred for 5 days at room temperature. The solvent was evaporated, and the residue was extracted with benzene (3 × 30 mL). Benzene was evaporated, and the residue obtained was purified by plate chromatography on SiO_2, eluent CH_2Cl_2. The fraction with R_f = 0.2−0.4 was separated and crystallized from pentane. Yield: 1.16 g (53%) of a light yellow powder. Mp: 118−119 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.33 (t, J = 7.5 Hz, 3H), 1.40 (d, J = 7 Hz, 12H), 1.47 (d, J = 7 Hz, 12H), 4.11 (sept., J = 7 Hz, 4H), 4.29 (q, J = 7 Hz, 2H), 7.5 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.76, 23.79 (d, J = 5.0 Hz), 24.01 (d, J = 2.5 Hz), 41.61, 49.48, 49.52, 126.01, 128.66, 129.23, 131.06, 151.38 (d, J = 8.8 Hz), 166.19 (d, J = 17.6 Hz). ^{31}P NMR (81 MHz, $CDCl_3$): δ 64.3. MS m/z (EI): 102.2, 132.2, 231.2, 249.4, 309.2, 311.2, 312.2, 459.2, 562.2, 563.2, 568.2. Anal. Calcd for $C_{22}H_{38}N_5PSe_2$ (561.46): C, 47.06; H, 6.82; N, 12.47. Found: C, 47.24; H, 6.69; N, 12.33.

Bis[1-(di-*tert*-butylphosphino)-4-ethyl-3-phenyl-1,2,4-triazol-5-ylidene]disilver(I) Bis(trifluoromethanesulfonate) (28b). Silver(I) oxide (0.28 g, 1.2 mmol) was added to a solution of compound **4b** (0.87 g, 1.9 mmol) in DCM (40 mL). The mixture was stirred for 2 h at 14 °C and then for 15 h at 29 °C. Then the precipitate was filtered and dissolved in acetonitrile (20 mL) at 100 °C (under a temperature higher than that stated, the complex undergoes decomposition). The hot solution was filtered. After the solution was cooled, the precipitate was filtered and washed with acetonitrile. Yield: 0.69 g (49%). Mp: 270 °C dec. ^{1}H NMR (500 MHz, CD_3CN): δ 1.54 (m, 42H), 4.42 (q, 4H), 7.65−7.80 (m, 10H). ^{13}C NMR (125 MHz, CD_3CN): δ 16.14, 28.02, 37.90, 44.42, 117.32, 121.16 (q, J = 320.6 Hz), 124.32, 129.33, 129.38, 131.82, 157.11. ^{31}P NMR (202 MHz, CD_3CN): δ 125.4 (d, J = 537 Hz). Anal. Calcd for $C_{38}H_{56}Ag_2F_6N_6O_6P_2S_2$ (1148.69): C, 39.73; H, 4.91; N, 7.32. Found: C, 39.65; H, 5.12; N, 7.06.

Bis[1-(di-*tert*-butylphosphino)-4-isopropyl-3-phenyl-1,2,4-triazol-5-ylidene]disilver(I) Bis(trifluoromethanesulfonate) (28c). Silver(I) oxide (0.22 g, 0.95 mmol) was added to a solution of compound **4c** (0.90 g, 1.9 mmol) in DCM (20 mL). The mixture was stirred for 20 h at 23 °C. The mixture was filtered, the filtrate obtained was evaporated, and the residue was recrystallized from ether (40 mL) and then acetonitrile (2 mL). Yield: 0.59 g (53%). Mp: 241−243 °C dec. ^{1}H NMR (500 MHz, CD_3CN): δ 1.55 (d, J = 17.5 Hz, 18H), 1.74 (d, J = 6.5 Hz, 6H), 4.78 (m, 1H), 7.6−7.8 (m, 5H). ^{13}C NMR (125 MHz, CD_3CN): δ 24.56, 28.08 (d, J = 10 Hz), 38.09, 51.22, 117.28, 121.21 (q, J = 320 Hz), 124.25, 129.35, 129.83, 131.85, 157.49. ^{31}P NMR (121 MHz, CD_3CN): δ 129.5 (d, J = 528.2 Hz). ^{19}F NMR (188 MHz, CD_3CN): δ −78.0. Anal. Calcd for $C_{40}H_{60}Ag_2F_6N_6O_6P_2S_2$ (1176.75): C, 40.83; H, 5.14; N, 7.14. Found: C, 40.52; H, 5.25; N, 7.33.

■ ASSOCIATED CONTENT

Supporting Information

Figures giving ^{1}H, ^{13}C, and ^{13}C APT NMR spectra for compounds **2**, **4a−d**, **5a−c**, **6a−d**, **7a−d**, **8a−d**, **9a−d**, **28b,c** and CIF files giving X-ray crystallographic data for **5c** and **28b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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