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A Convenient Approach to *N*-(Di-*tert*-butylphosphanyl)- and *N*-(Di-*tert*-butylphosphoroselenoyl)formamidinium Salts: Carbene Precursors

Anatoliy Marchenko,[a] Georgyi Koidan,[a] Anastasiya Hurieva,[a] Aleksandr Savateev,[a] Alexander B. Rozhenko,[a] Jean-Marc Sotiropoulos,[b] Svitlana V. Shishkina,[c] Oleg V. Shishkin,[c,d] and Aleksandr Kostyuk*[a]

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The reactions of (di-*tert*-butylphosphanyl)amines and *P,P*-di-*tert*-butylphosphinoselenoic amides with Alder's dimer were studied. For di-*tert*-butylphosphanylamines, the reaction proceeds by primary electrophilic attack of Alder's dimer at the phosphorus atom to afford a dicationic salt **3**. The deprotonation of **3** led to *N*-phosphanylformamidine **5** ("phosfam"). Alkyl(di-*tert*-butylphosphanyl)amines reacted with Alder's dimer in a 2:1 molar ratio to give *N*-phosphanylformamidinium salts; the second equivalent of (alkylamino)phosphane acts as a base. (Arylamino)phosphanes reacted with Alder's dimer to give benzazaphospholium derivatives. To direct the electrophilic attack of Alder's dimer at the nitrogen atom, phosphinoselenoic amides were used. They reacted with Alder's dimer at the selenium atom followed by a selenium–phosphorus shift to give *N*-(di-*tert*-butylphosphoroselenoyl)formamidinium salts. The phosphinoselenoic amides with bulky substituents (adamantyl, *t*Bu) underwent cleavage of the N–alkyl bond to afford phosfams. Various key intermediates such as **3** and **22b** were isolated and characterized. A convenient method for the synthesis of carbene precursor P^{III} and P^{V} *N*-substituted formamidinium salts was developed.

Introduction

Among the available approaches to carbenes, the most common synthetic route is the deprotonation of cationic heterocycles or acyclic iminium salts. Their design and synthesis constitute the main challenge, as the method works quite well. Recent reviews focus on their synthesis and the subsequent carbene preparation.[1]

Recently, it has been shown that *N*-phosphanyl-substituted N-heterocyclic carbenes (NHCP ligands) derived from imidazole, benzimidazole, and triazole can be isolated as discrete compounds.[2] The main approach to NHCP ligands is based on the deprotonation of *N*-(di-*tert*-butylphosphanyl)azolium triflates. These salts were prepared by treating *N*-substituted azoles with bromodi-*tert*-butylphosphane in tetrahydrofuran (THF) in the presence of sodium triflate. The NHCP ligands were employed in the synthesis of transition metal complexes either from their silver complexes[3] or directly by reactions with metal salts.[4] These complexes have shown promising activity in nitrene transfer reactions.[3] The stability of NHCP ligands **A** (Figure 1) is significantly dependent on the bulkiness of the substituents at the phosphorus atom, and the di-*tert*-butylphosphanyl group provides the most stable ligands.

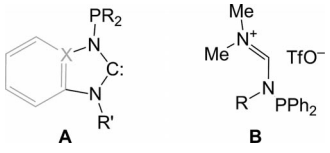

Figure 1. Available NHCP ligands and *N*-phosphanylformamidinium salts.

Continuing our research on the synthesis of analogous acyclic *N*-phosphanyl carbenes, we applied the well-developed method for the synthesis of *N*-phosphanylazolium triflates to *N*,*N*-dialkyl-*N*′-aryl(alkyl)formamidines. New *N*-phosphanylformamidinium salts of type **B** were synthesized by the reaction of *N*,*N*-dialkyl-*N*′-aryl(alkyl)formamidines with bromodiphenylphosphane in tetrahydrofuran in the presence of sodium triflate (Figure 1).[5] It should be noted that *N*,*N*-dialkyl-*N*′-aryl(alkyl)formamidines do not react

[a] Institute of Organic Chemistry, National Academy of Sciences of Ukraine,
Murmanska 5, 02660 Kyiv 94, Ukraine
www.ioch.kiev.ua
[b] CNRS/Univ. de Pau & des Pays de l'Adour, IPREM, UMR 5254,
2 Avenue du Président P. Angot, 64053 Pau cedex 09, France
[c] SSI "Institute for Single Crystals", National Academy of Sciences of Ukraine,
Lenin ave. 60, 61001 Kharkiv 01, Ukraine
[d] Department of Inorganic Chemistry, V. N. Karazin Kharkiv National University,
4 Svobody sq., Kharkiv 61202, Ukraine
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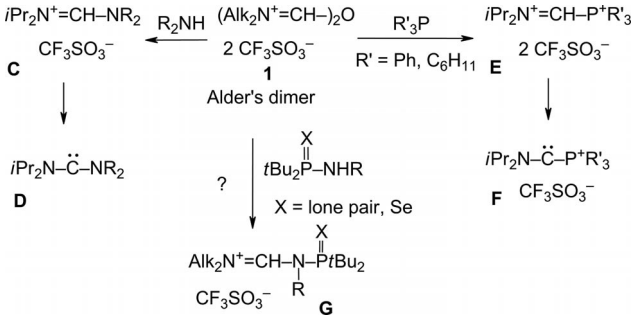
with the more bulky bromodi-*tert*-butylphosphane under the same conditions. The deprotonation of these salts **B** gave *C*-phosphanylformamidines via intermediate carbenes that were identified spectroscopically and trapped by reaction with selenium. The failure to prepare stable carbenes indicates that more kinetic stabilization is required to provide stability to carbenes of this type. Therefore, other approaches to *N*-phosphanylformamidinium salts bearing bulky groups at the phosphorus atom should be developed. Alder and co-workers[6a,6b] have introduced into synthetic practice new powerful reagents **1** (Alder's dimer) that can be readily prepared by the reaction of *N*,*N*-dialkylformamides with triflic anhydride. They react more cleanly and in higher yields compared to Vilsmeier–Haack congeners.[6c]

Alder's dimer reacts readily with primary and secondary amines to give trialkyl- or tetraalkylformamidinium salts **C**, respectively (Scheme 1). The first stable acyclic diaminocarbene **D** (R = *i*Pr) was prepared in 1996 by Alder by this approach.[7] Bertrand et al. utilized it in the reaction with phosphanes for the preparation of the carbene precursors **E** and carbenes **F**.[8]



Scheme 1. Reactions of Alder's dimer with amines and phosphanes.

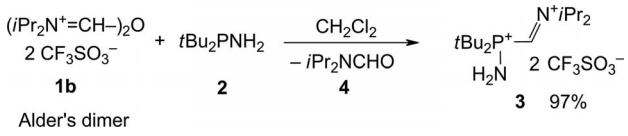
The data presented above allowed us to suppose that access to the previously unknown *N*-phosphanylformamidinium and *N*-(phosphoroselenoyl)formamidinium salts **G**, the precursors for the corresponding carbenes, would be provided by the (dialkylamino)methylation of aminodi(*tert*-butyl)phosphanes or di-*tert*-butylphosphoroselenoyl amides.

Results and Discussion

1. Reactions of Alder's Dimer with Aminophosphanes

1.1 Aminodi(tert-butyl)phosphane

Amino(diorganyl)phosphanes are labile compounds prone to dimerization under elimination of ammonia.[9] These species can be stabilized by the introduction of bulky substituents at the phosphorus atom. For instance, aminodi(*tert*-butyl)phosphane (**2**) is quite a stable compound. Similarly to Ph_3P, aminophosphane **2** was found to react readily with Alder's dimer **1b** in a 1:1 molar ratio to afford the dicationic salt **3** (Scheme 2). The ^{31}P NMR spectrum of the reaction mixture exhibited one singlet at δ = 66 ppm.



Scheme 2. Reaction of aminophosphane **2** with **1b**.

Compound **3** is a moisture-sensitive, colorless, crystalline substance. The structure of **3** was proved by ^1H and ^{13}C NMR spectroscopy and X-ray diffraction analysis (Figure 2).

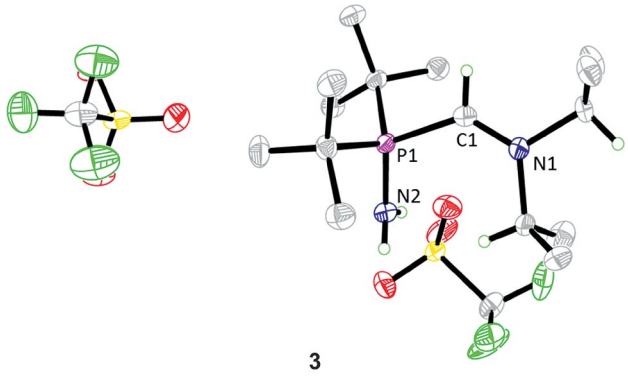
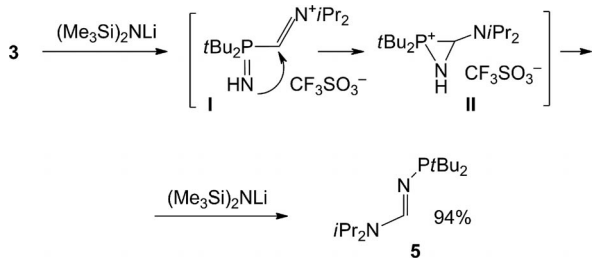


Figure 2. Molecular structure of **3** according to the X-ray diffraction data. Here and in the following structure representations, the thermal ellipsoids of atoms are shown at 50% probability levels. Some hydrogen atoms are omitted for clarity.

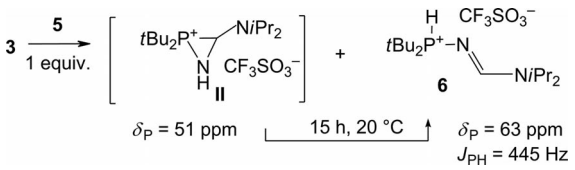
The N1 atom forms two N–C(*i*Pr) single bonds and the C1–N1 bond, the length of which [1.277(3) Å] is even shorter than the mean value for C(sp^2)=N(3) double bonds (1.316 Å).[10] The tetracoordinated phosphorus atom forms three P1–C single bonds and one P1=N2 double bond [the length of 1.606(2) Å is close to the mean value (1.599 Å) for P=N double bonds]. Quantum chemical calculations (RIJCOSX-B3LYP-D3/TZVP) yield a similar structure for the dicationic part of **3** [*d*(C=N) = 1.276 Å, *d*(C–P) = 1.870 Å, ∠(PCN) = 134.2°]. The natural population analysis (NPA) at the B3LYP/TZVP level of theory predicted the double bond of the C=N($iPr)_2$ moiety (calculated Wiberg bond order 1.78) but a slightly negative total charge on the nitrogen atom (–0.19 e) and delocalization of only +0.52 e on the N($iPr)_2$ fragment.

Compounds of type **E** can be deprotonated with 1 equiv. of lithium bis(trimethylsilyl)amide to give stable carbenes of phosphonium type **F** (Scheme 1) as shown by Bertrand.[8] If salt **3** is deprotonated with 2 equiv. of base, *N*-phosphanylformamidine **5** is formed (Scheme 3). This type of hardly accessible compounds (named "phosfams") was recently prepared by the reaction of iPr_2NCN with chlorophosphanes R_2PCl (R = iPr_2N, Ph, Et, *i*Pr) in the presence of 1 equiv. of hydridozirconocene.[11] Phosfam **5** is an air-sensitive, colorless, crystalline compound. It possesses a *trans* configuration, as evidenced by its ^1H and ^{13}C NMR spectra, which are similar to those of the previously described *i*Pr analogue.[11]



Scheme 3. Synthesis of phosfam **5**.

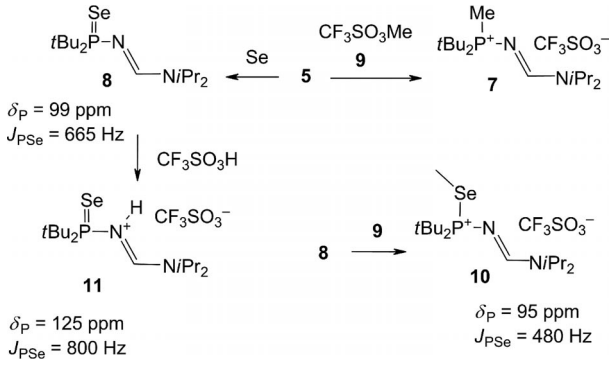
The formation of phosfam **5** can be rationalized by the nucleophilic attack of the carbocationic center by the nitrogen atom of the iminophosphane **I** formed upon deprotonation of salt **3** (Scheme 3). Further deprotonation of the phosphoniaaziridine **II** led to the cleavage of the P–C bond to afford phosfam **5**. Our attempts to identify these intermediates failed. When phosfam **5** itself (1 equiv.) was used for the deprotonation of salt **3**, the ^{31}P NMR spectra of the reaction mixture exhibited a doublet for **6** at δ_P = 63 ppm ($J_{P,H}$ = 445 Hz) and a singlet at δ_P = 51 ppm. The latter transformed completely into the doublet of **6** at room temperature in 15 h (Scheme 4).



Scheme 4. Deprotonation of salt **3** with phosfam **5**.

Therefore, the signal at δ_P = 51 ppm can be assigned to phosphoniaaziridine **II**. This is in line with the stepwise nature of the formation of phosfam **5** from salt **3**.

Although *N*-alkyl(aryl)formamidines are alkylated at the sp^2 nitrogen atom to afford formamidinium salts, which are carbene precursors,[12] *N*-phosphanylformamidines are alkylated only at the phosphorus atom.[11] Even the presence of bulky *tert*-butyl groups at the phosphorus atom does not change the course of the reaction, and **5** was also alkylated at the phosphorus atom to afford the phosphonium salt **7** (Scheme 5). Our approach to direct alkylation at the sp^2 nitrogen atom by oxidation of phosfam **5** with selenium failed, as **8** was alkylated at the selenium atom to afford salt **10**, which exhibited a coupling constant of $^1J_{P,Se}$ = 480 Hz, typical for a single P–Se bond, in the ^{31}P NMR spectrum.[13]



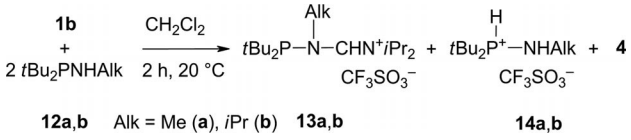
Scheme 5. Attempts to prepare *N*-phosphanylformamidinium salts from phosfam **5**.

At the same time, the protonation of **8** with triflic acid proceeded at the imine nitrogen atom to give **11**. This was confirmed by a coupling constant ($^1J_{P,Se}$ = 800 Hz) typical for a P=Se double bond and by the doublet of doublets for the CH proton ($^3J_{P,H}$ = 13.2 Hz, $^3J_{H,H}$ = 9.6 Hz) in the ^1H NMR spectrum.

1.2 (Alkylamino)di(tert-butyl)phosphanes

As the *N*-phosphanylformamidines cannot serve as starting materials for the synthesis of the target salts, we deemed it appropriate to investigate the reaction of Alder's dimer with phosphanes bearing a secondary amine group at the phosphorus atom.

(Alkylamino)di(*tert*-butyl)phosphanes **12** reacted with Alder's dimer in a 2:1 molar ratio, and the second equivalent of aminophosphane acted as a base (Scheme 6). The mechanism for the formation of **13** is probably the same as that for the formation of phosfam **5**, in which primary electrophilic attack of Alder's dimer at the phosphorus atom affords an intermediate of type **3**. The intermediate is further deprotonated by a second molecule of aminophosphane to give compounds **13**, which are white, moisture-sensitive solids. The ^1H and ^{13}C NMR spectra are consistent with the proposed structures. The structures of **13a** and **13b** were confirmed by X-ray diffraction analyses (Figure 3). The positive charges in both compounds are partially located at the N1 atom, which forms two single N–C(*i*Pr) bonds and one double bond [C1=N1 1.307(1) Å in **13a** and 1.308(3) Å in **13b**] similar to that in **3**. In **13a**, the positive charge is delocalized on the N(*i*Pr)$_2$ group (+0.22 e), the central CH fragment (+0.57 e), and N(Me)[P(*t*Bu)$_2$] (the remainder). This is in line with the partially double-bond character of the two N1–C(H)–N2(*i*Pr)$_2$ bonds (the calculated Wiberg bond indices are 1.39 and 1.42 for the C–N1 and C–N2 bonds, respectively), which correspond to the longer calculated C–N2 bond than that in **3**.



Scheme 6. Reaction of (alkylamino)phosphanes **12** with Alder's dimer **1b**.

Notably, the ^{31}P NMR spectrum for **13a** has three broadened peaks, whereas two signals are observed in the spectrum of **13b** at room temperature. At 80 °C, coalescence occurred (Figure 4) to give one broad peak at $\delta \approx 138$ ppm. On cooling, identical spectra were observed.

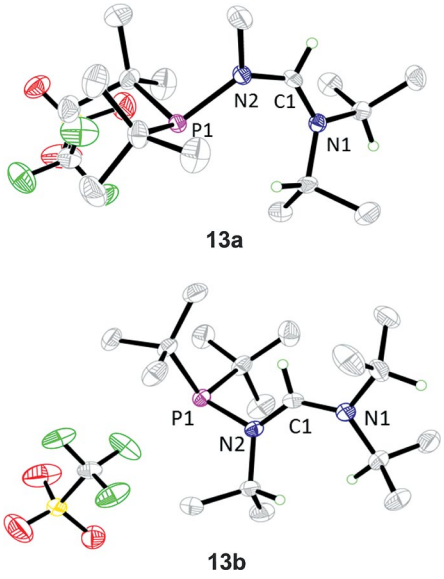


Figure 3. Molecular structures of **13a** and **13b** according to the X-ray diffraction data.

Initially, we assumed that the three signals in the ^{31}P NMR spectrum for **13a** resulted from its equilibrium with two linear forms **13-I** and **13-III** via the phosphoniaaziridine intermediates **13-II** (Figure 5).

Quantum chemical (DFT) calculations for a set of compounds **13a**–**13c** [R = Me (**13a**), *i*Pr (**13b**), and mesityl (Mes; **13c**)] indicated that for these three derivatives, the isomer **I** is the most stable one, followed by **III** and **II**. The differences in energy between **I** and **II** and between **I** and **III** are particularly large in the case of **13a** (70.6 and 59.5 kcal/mol, respectively). For **13b** and **13c**, these differences are 21–33 kcal/mol (see Supporting Information for details). Therefore, an equilibrium between **13-I** and **13-II** (**13-III**) and even between **13-II** and **13-III** seems to be unlikely. At the same time, calculations predict a very close thermodynamic stability (ΔG within 1.3 kcal/mol) for three conformations of **13** (Figure 6; **13aA**, **13aB**, and **13aC**). Thus, the three different signals at room temperature in the experimental ^{31}P NMR spectra (Figure 4) can be attributed to the simultaneous existence of the three above-mentioned rotamers in solution. The process probably corresponds to the exchange between three conformations **13aA**–**13aC** by a hindered rotation about the N–P and (P)N–C bonds. The

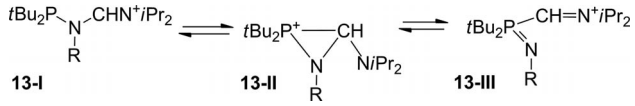


Figure 5. Possible equilibrium responsible for the multiple signals in the ^{31}P NMR spectra of **13**.

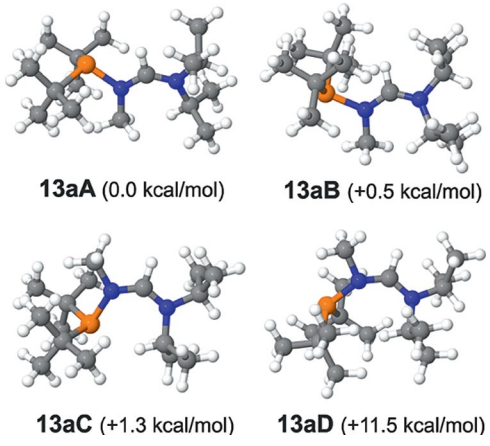


Figure 6. Jmol plots of equilibrium structures and relative energies (RIJCOSX-B3LYP-D3/TZVP) for different conformations of **13a**.

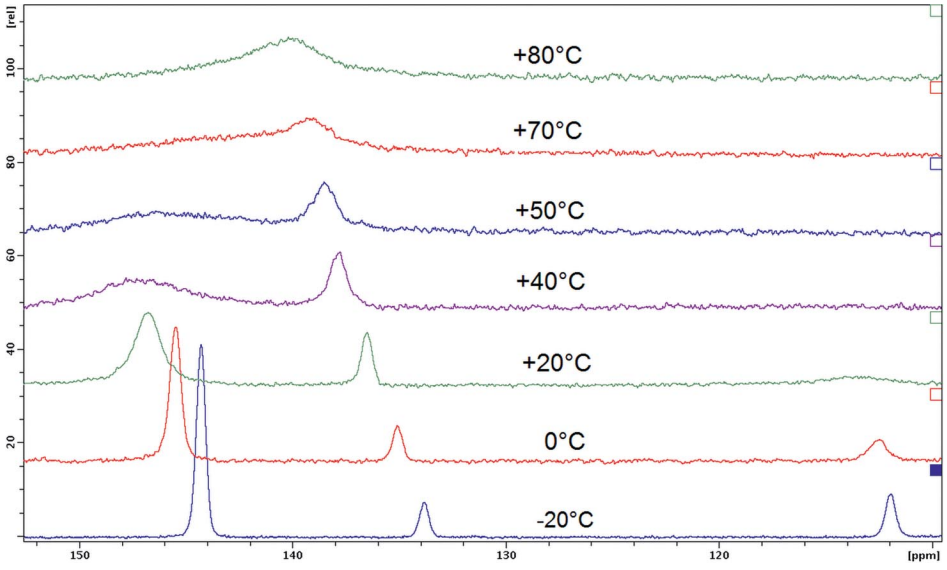
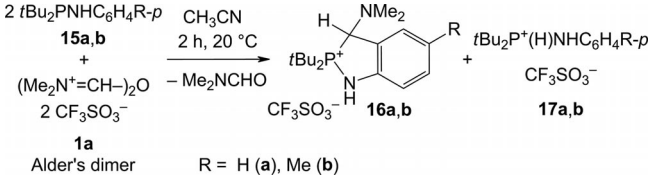


Figure 4. ^{31}P NMR spectra of **13a** from –20 (bottom) to 80 °C (top).

latter clearly possesses a partially double-bond character (Figure 6). In contrast, structure **13aD** is definitely less favorable and should be excluded from consideration.

1.3 (Arylamino)di(tert-butyl)phosphanes

Like (alkylamino)phosphanes **12**, (arylamino)phosphanes **15** reacted with Alder's dimer **1a** in a 2:1 molar ratio but afforded cyclic compounds **16** and triflic salts **17** (Scheme 7).



Scheme 7. Reaction of (arylamino)phosphanes **15** with Alder's dimer **1a**.

Compounds **16** are air-stable crystalline solids. The structure of **16a** was elucidated by ^{1}H and ^{13}C NMR spectroscopy and X-ray diffraction analysis (Figure 7). Analysis of the bond lengths in both molecules of **16a** (**16a-A** and **16a-B**) located in the asymmetric part of the crystal unit cell demonstrates that the phosphorus atom forms four single bonds (three P–C bonds and one P–N bond). In contrast to **3**, **13a**, and **13b**, the lengths of the P–N bonds in **16a-A** and **16a-B** [1.654(5) and 1.658(4) Å, respectively] correspond to the mean value of the P(4)–N(3) single bond (1.662 Å). Therefore, it can be assumed that the positive charge in cation **16a** is localized at the phosphorus atom.

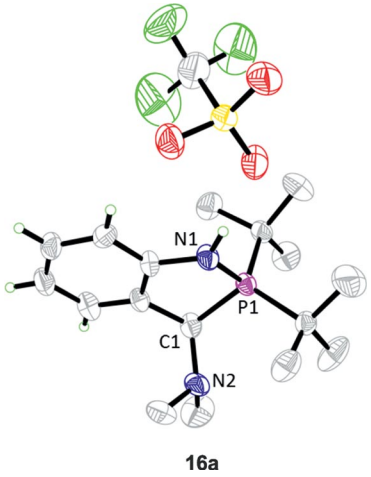
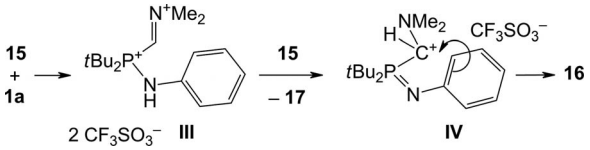


Figure 7. Molecular structure of **16a** according to X-ray diffraction data.

Similarly to other aminophosphanes, the formation of **16** probably proceeded by generation of dicationic salt **III**, which was deprotonated with a second equivalent of aminophosphane **15** to afford intermediate **IV** (Scheme 8). The latter cyclized by a carbocationic mechanism similar to that for *N*-aryl(pyrazolyl)phosphinimidic isocyanates.[14]

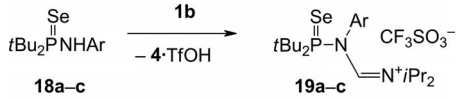


Scheme 8. Possible intermediates in the formation of **16**.

2. Reactions of Phosphinoselenoic Amides with Alder's Dimer

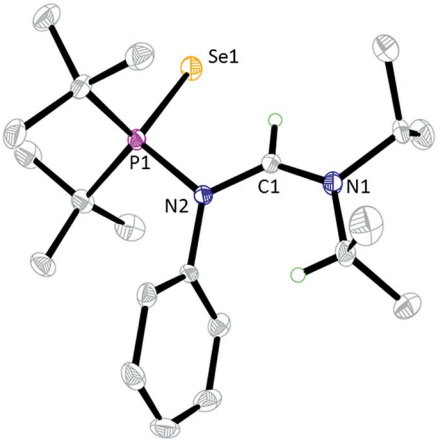
2.1 N-Arylphosphinoselenoic Amides

As the reactions of Alder's dimer with aminophosphanes **2**, **12**, and **15** proceed at the phosphorus atom, one might expect that its protection would change the direction of the reaction towards the amino group. Indeed, **18a–c** reacted readily with Alder's dimer **1b** in a 1:1 molar ratio to give salts **19a–c** and the triflic salt of formamide **4** (Scheme 9). The latter is sparsely soluble in diethyl ether, allowing its complete separation from salts **19**. Alternatively, after removal of the solvent, the residue can be treated with water to remove the triflic salt of formamide **4**.

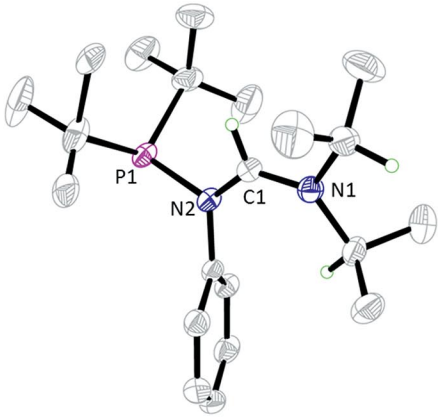


Scheme 9. Reaction of phosphinoselenoic amides **18** with Alder's dimer **1b**.

Salts **19** are colorless, crystalline, air-stable compounds, which were unambiguously characterized by elemental analyses and spectroscopic methods and additionally by X-ray diffraction analysis for **19a** (Figure 8). They were readily reduced with $(Me_2N)_3P$ to give the previously unknown salts **20a–c** (Scheme 10). According to the X-ray diffraction data, the N1 atom forms two N–C(*i*Pr) single bonds and one shortened C1–N1 bond [1.305(2) Å] in **19a** and **20a**. In both cases, similar charge distributions were found. In **19a** and **20a**, the most positive charge is localized on the central CH moieties (+0.59 e in both cases), and much less is concentrated on the N(*i*Pr)$_2$ group (+0.25 and +0.23 e, respectively). Again, the N1–C(H) and C(H)–N2(*i*Pr)$_2$ bonds are shortened (1.338 and 1.307 Å, respectively, in **19a** and 1.334 and 1.312 Å, respectively, in **20a**) and have partially double-bond character [calculated bond orders for **19a**: 1.32 (1.36 in **20a**) and 1.46 (1.44 in **20a**) for the N1–C(H) and C(H)–N2 bonds, respectively].

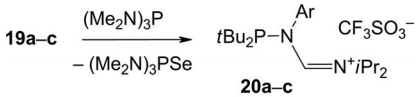


19a



20a

Figure 8. Molecular structures of **19a** and **20a** according to the X-ray diffraction data. The triflate anions are omitted for clarity.



Ar = Ph (**a**), 4-MeC$_6$H$_4$ (**b**), 4-MeOC$_6$H$_4$ (**c**)

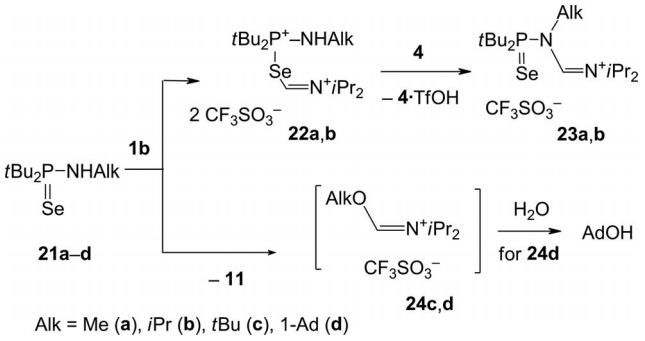
Scheme 10. Reduction of salts **19**.

Compounds **20a**–**c** are colorless, moisture-sensitive, crystalline compounds, the structures of which were confirmed by ^{1}H and ^{13}C NMR spectroscopy.

2.2 N-Alkylphosphinoselenoic Amides

To extend our method for the synthesis of salts **19**, we investigated the reaction of Alder's dimer with *N*-alkyl-substituted phosphinoselenoic amides **21a**–**d** (Scheme 11).

The *N*-alkylphosphinoselenoic amides **21** reacted more slowly than the *N*-aryl derivatives **18**, probably because of the lower acidity of the amide hydrogen atom. Moreover, the rate and composition of the products of the reaction depended dramatically on the bulkiness of the alkyl substituent. Thus, the reactions of **21c** and **21d** [*t*Bu, adamantyl



Alk = Me (**a**), *i*Pr (**b**), *t*Bu (**c**), 1-Ad (**d**)

Scheme 11. Reaction of phosphinoselenoic amides **21** with Alder's dimer **1b**.

(Ad)] are irreversible and were complete at 25 °C after 3 h to give triflate salt **11** and probably salts **24c** and **24d**, as an alkaline hydrolysis of **24d** after separation of **11** gave AdOH. In contrast, the reactions of **21a** and **21b** (Me, *i*Pr) led to salts **23a** and **23b**, but the reaction proceeded very slowly; 30 min after the reactants were mixed, the ^{31}P NMR spectra exhibited weak signals of the salts **23a** and **23b**, the starting compounds **21a** and **21b**, and strong signals of intermediates at δ_P = 112 (**22a**) and 106 ppm (**22b**) with $J_{P,Se}$ 350–380 Hz, typical for P–Se single bonds. Eventually, the intensity of the signals of **23a** and **23b** increased, and the intensity of the other signals decreased. The final spectral yields of the salts reached 89% in 30 h for **23a** and 71% in 72 h for **23b**. Therefore, we could conclude that Alder's dimer reacted with phosphinoselenoic amides **18** and **21** at the selenium atom to afford the dicationic salts of type **22** and diisopropylformamide **4**. The latter deprotonated salt **22** to initiate a [1,3] shift of the aminomethylene group from the selenium atom to the nitrogen atom. We successfully isolated the intermediate **22b**. It is a transparent, crystalline, moisture-sensitive solid. The structures of intermediate **22b** and compound **23b** were confirmed by X-ray diffraction analyses (Figure 9). Analysis of the bond lengths in intermediate **22b** indicates that both nitrogen atoms form two single bonds [two N–C(*i*Pr) bonds for the N1 atom and N–C(*i*Pr) and N–H bond for the N2 atom] and short N1=C1 [1.275(6) Å] and N2=P1 bonds [1.616(3) Å]. Despite the very short calculated C=N(*i*Pr)$_2$ bond length (1.283 Å), one of the two positive charges in **22** is only partly located on the N(*i*Pr)$_2$ moiety (+0.42 e) and, hence, the proposed mesomeric form with the positively charged nitrogen atom is not fully correct (the total charge on N2 is –0.26). The almost full positive charge unit (+0.85) is delocalized within the SeC(H)N2(*i*Pr)$_2$ fragment. The calculated Wiberg bond indices for the C–N and Se–C bonds (1.64 and 1.17, respectively) also indicate participation of the nitrogen and selenium atoms in the positive charge delocalization. The second positive charge is concentrated on the phosphorus atom.

In contrast to **13** and **19**, in **23**, the calculated bond lengths and Wiberg bond indices for C–N1 and C–N2 in the N1–C(H)–N2(*i*Pr)$_2$ moiety differ significantly (1.296 and 1.405 Å, 1.53 and 1.05, respectively). The P1 environment is almost orthogonal to the CH–N2 π-system. The

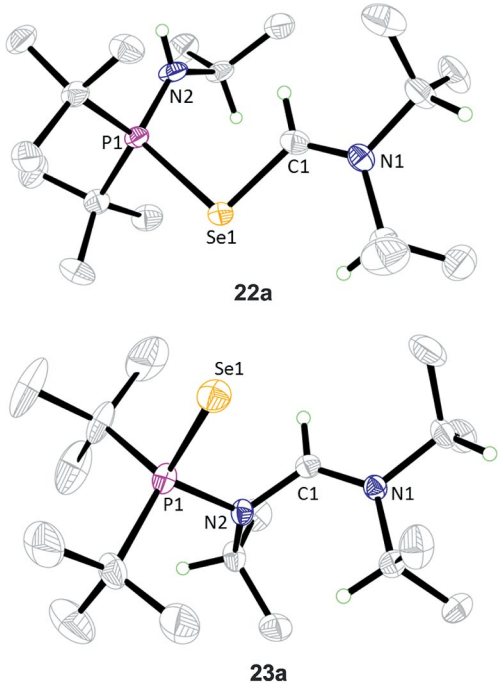


Figure 9. Molecular structures of **22b** and **23b** according to the X-ray diffraction data. Triflate anions are omitted for clarity.

positive charge (+0.91 e) is delocalized in the C(H)–N2-(iPr)$_2$ moiety, and its largest part is concentrated on the central carbon atom. Thus, the structure of **23** is best represented by the Lewis structure with the positive charge at the carbon atom.

Conclusions

We have developed a convenient approach to *N*-phosphanyl- and *N*-(phosphoroselenoyl)formamidinium salts from the reactions of aminophosphanes or phosphinoselenoic amides with Alder's dimer. For the aminophosphanes, the primary electrophilic attack of Alder's dimer proceeded at the phosphorus atom. The subsequent reaction course depended on the substituents at the nitrogen atom. The aminophosphane bearing an NH_2 group gave the aminophosphonium salt **3**, which, upon treatment with a base, rearranged into neutral phosfam **5**. The aminophosphanes bearing an NHAlkyl group reacted with Alder's dimer in a 2:1 molar ratio. The reaction proceeded at the phosphorus atom, and the second equivalent of aminophosphane acted as a base to induce the rearrangement to the final *N*-phosphanylformamidinium salt. The aminophosphane bearing an NHPh group also reacted at the phosphorus atom followed by cyclization to form benzazaphospholium derivatives. Phosphinoselenoic amides reacted with Alder's dimer at the selenium atom. Depending on the substituents at the nitrogen atom, these intermediates behaved differently. *N*-Aryl- and *N*-alkyl- (Me, *i*Pr) -phosphinoselenoic amides readily gave formamidinium salts, and the latter reacted more slowly. The phosphinoselenoic amides with bulky substituents (Ad, *t*Bu) underwent cleavage of the N–alkyl bond to afford phosfams. The developed method makes the carbene precursor formamidinium salts bearing either a tri- or pentavalent phosphorus group at the nitrogen atom readily available. Deprotonation of the formamidinium salts is under investigation and will be reported separately.

Experimental Section

General: All procedures with air- and moisture-sensitive compounds were performed under dry argon in flame-dried glassware. Solvents were purified and dried by standard methods. Melting points were determined with an electrothermal capillary melting point apparatus. ^{1}H NMR spectra were recorded with a Bruker Avance DRX 500 (500.13 MHz) or a Varian VXR-300 (299.94 MHz) spectrometer. ^{13}C NMR spectra were recorded with a Bruker Avance DRX 500 (125.75 MHz) spectrometer. ^{31}P NMR spectra were recorded with a Varian VXR-300 (121.42 MHz) or a Bruker Avance 400 spectrometer (161.98 MHz). Chemical shifts (δ) are reported in ppm downfield relative to internal tetramethylsilane (TMS) for ^{1}H and ^{13}C and external 85% H_3PO_4 for ^{31}P. Chromatography was performed on Gerudan SI60 silica gel. Elemental analyses were performed at the analytical laboratory of the Institute of Organic Chemistry, National Academy of Sciences of Ukraine.

Calculations: All structures were optimized by using Gaussian 09[15] (see Supporting Information) and the ORCA program package (version 2.9).[16] The B3LYP[17,18] hybrid functional including the last version of Grimme's correction for dispersion interactions (B3LYP-D3)[19] and TZVP basis sets (the TZV basis sets of triple-zeta quality[20] plus one p function set for hydrogen atoms or one d function set for all other atoms). For more efficient calculations, the parallel RIJCOSX algorithm[21,22] was used with the accurate grid parameters (Grid5, GridX6). The vibrational frequencies were calculated numerically, and no imaginary frequencies were found for the equilibrium geometries. The relative energies (ΔG) were calculated by using total energy values corrected for Gibbs free energy; no scaling was used. The NPA charges and Wiberg indices[23] were calculated by using the natural bond orbital (NBO) procedure (version 3.1) implemented in the Gaussian 09 set of programs. The structures were presented graphically by using the Jmol program.[24]

Single-Crystal X-ray Diffraction Analysis: X-ray diffraction analyses were performed with automatic Bruker APEX II (**3**, **13a**, **13b**, **16**, **20a**, **22b**, and **23b**) and Xcalibur 3 (**19a**) diffractometers (graphite-monochromated Mo-K_α radiation, CCD detector, ω-scanning). The structures were solved by direct methods by using the SHELXTL package.[25] The positions of the hydrogen atoms were located from electron-density difference maps and refined in isotropic approximations, except for **16**, for which the hydrogen atoms were refined by a "riding" model with $U_{iso} = nU_{eq}$ of the carrier atom (n = 1.5 for methyl groups and n = 1.2 for other hydrogen atoms). The crystallographic data and experimental parameters are listed in Table S1. CCDC-928575 (for **3**), -959126 (for **13a**), -959127 (for **13b**), -928576 (for **16**), -959128 (for **19a**), -959129 (for **20a**), -959130 (for **22b**), and -959131 (for **23b**) contain the crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Diisopropyl[amino(di-*tert*-butyl)phosphonio]methyleneammonium Bis(trifluoromethanesulfonate) (3): To a suspension of **1b** (0.01 mol) in dichloromethane (DCM; 30 mL) cooled to –10 °C was added a solution of **2** (0.01 mol) in DCM (30 mL) with stirring. A solid

precipitated over 5 min. The reaction mixture was stirred at 20 °C for 1 h. The precipitate was collected by filtration, washed twice with DCM, and dried in vacuo to give a white solid (5.54 g, 97%); m.p. 160–162 °C (CH_3CN). ^{31}P NMR (CD_3CN): δ = 66.2 ppm. ^1H NMR (CD_3CN): δ = 1.57 (d, $J_{P,H}$ = 18.3 Hz, 18 H, CH_3), 1.63 (d, $J_{H,H}$ = 6.6 Hz, 12 H, CH_3), 4.86 (m, 1 H), 5.56 (m, 1 H), 5.93 (d, $J_{P,H}$ = 6 Hz, 2 H, NH_2), 9.1 (d, $J_{P,H}$ = 30 Hz, 1 H, CH) ppm. ^{13}C NMR (CD_3CN): δ = 19.3 (s, CH_3), 23.1 (s, CH_3), 25.6 (s, CH_3), 37.4 (d, $J_{C,P}$ = 47 Hz), 62.8 (d, $J_{C,P}$ = 4 Hz, CH), 63.7 (d, $J_{C,P}$ = 4 Hz, CH), 120.9 (q, $J_{C,F}$ = 321 Hz, CF_3), 171.7 (d, $J_{C,P}$ = 28 Hz, CH) ppm. $C_{17}H_{35}F_6N_2O_6PS_2$ (572.56): calcd. C 35.66, H 6.16, N 4.89, P 5.41; found C 35.23, H 5.97, N 4.97, P 5.17.

***N′*-(Di-*tert*-butylphosphanyl)-*N*,*N*-diisopropylformamidine (5):** To a suspension of **3** (5 mmol) in THF (20 mL) cooled to –10 °C was added a solution of $(Me_3Si)_2NLi$ (10 mmol) with stirring over 5 min. The reaction mixture was stirred for 10 min, and then the THF was evaporated. Pentane (15 mL) was added to the residue, and the solid precipitate was removed by filtration and washed with pentane. The filtrate was concentrated, and the residue was distilled to give colorless crystals (1.28 g, 94%); b.p. 60–63 °C/5 Torr, m.p. 37–39 °C. ^{31}P NMR (C_6D_6): δ = 102.5 ppm. ^1H NMR (C_6D_6): δ = 0.81 (d, $J_{H,H}$ = 6.9 Hz, 6 H, CH_3), 1.12 (d, $J_{H,H}$ = 6.9 Hz, 6 H, CH_3), 1.27 (d, $J_{P,H}$ = 10.5 Hz, 18 H, CH_3), 2.97 (m, 1 H, CH), 4.30 (m, 1 H, CH), 8.1 (d, $J_{P,H}$ = 18.0 Hz, 1 H, CH) ppm. ^{13}C NMR (C_6D_6): δ = 19.9 (s, CH_3), 22.8 (s, CH_3), 28.4 (d, $J_{C,P}$ = 14 Hz, CH_3), 32.9 (d, $J_{C,P}$ = 20 Hz, C), 44.8 (s, CH), 47.2 (s, CH), 157.5 (d, $J_{C,P}$ = 39 Hz, CH) ppm. $C_{15}H_{33}N_2P$ (272.41): calcd. C 66.14, H 12.21, N 10.28, P 11.37; found C 65.78, H 12.01, N 10.15, P 11.58.

Di-*tert*-butyl{[(diisopropylamino)methylene]amino}phosphonium Trifluoromethanesulfonate (6): To a suspension of **3** (25 mmol) in THF (10 mL) at 20 °C was added a solution of **5** (25 mmol) in THF (5 mL) with stirring. In 30 min, the ^{31}P NMR spectrum of the reaction mixture exhibited signals at δ = 51 and 63 ppm ($J_{P,H}$ = 445 Hz). The solvent was evaporated, and diethyl ether (20 mL) was added. The precipitated solid was collected by filtration, washed with diethyl ether (3× 15 mL), and dried. Yield 1.9 g (90%); m.p. 88–89 °C. ^{31}P NMR (CD_3CN): δ = 63 ($J_{P,H}$ = 445 Hz) ppm. ^1H NMR (CD_3CN): δ = 1.29 (d, $J_{H,H}$ = 6.9 Hz, 6 H, CH_3), 1.30 (d, $J_{H,H}$ = 6.9 Hz, 6 H, CH_3), 1.31 (d, $J_{P,H}$ = 16.8 Hz, 18 H, CH_3), 3.86 (m, 1 H, CH), 4.47 (m, 1 H, CH), 6.31 (d, $J_{P,H}$ = 428 Hz, 1 H, PH), 8.03 (d, $J_{P,H}$ = 20.7 Hz, 1 H, CH) ppm. $C_{16}H_{34}F_3N_2O_3PS$ (422.48): calcd. N 6.63, P 7.33; found N 6.96, P 7.22.

Di-*tert*-butyl{[(diisopropylamino)methylene]amino}(methyl)phosphonium Trifluoromethanesulfonate (7): To a solution of **5** (2.5 mmol) in DCM (5 mL) at –78 °C was added a solution of methyl trifluoromethanesulfonate (2.5 mmol) in DCM (5 mL) with stirring. After 10 min, the temperature was increased to 20 °C, and the solvent was evaporated. The remaining solid was washed with diethyl ether (2× 5 mL) and dried. Yield 0.88 g (81%); m.p. 78–79 °C, colorless crystals. ^{31}P NMR ($CDCl_3$): δ = 59 ppm. ^1H NMR ($CDCl_3$): δ = 1.23 (d, $J_{P,H}$ = 15 Hz, 18 H, CH_3), 1.24 (d, $J_{H,H}$ = 8 Hz, 3 H, CH_3), 1.28 (d, $J_{P,H}$ = 6.5 Hz, 6 H, CH_3), 1.79 (d, $J_{P,H}$ = 6.5 Hz, 6 H, CH_3), 3.91 (m, 1 H, CH), 4.07 (m, 1 H, CH), 7.92 (d, $J_{P,H}$ = 19 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 0.4 (d, $J_{C,P}$ = 42 Hz, CH_3), 19.7 (s, CH_3), 22.0 (s, CH_3), 26.0 [s, $(CH_3)_3$], 34.6 (d, $J_{C,P}$ = 62 Hz, C), 46.8 (s, CH), 52.3 (s, CH), 158.6 (s, CH) ppm. MS: *m*/*z* = 287 [M – $CF_3SO_3^-$]$^+$. $C_{17}H_{36}F_3N_2O_3PS$ (436.51): calcd. C 46.78, H 8.31, N 6.42, P 7.10; found C 47.11, H 8.47, N 6.37, P 6.89.

***N*,*N*-Diisopropyl-*N′*-(di-*tert*-butylphosphoroselenoyl)formamidine (8):** To a solution of **5** (2.5 mmol) in benzene (5 mL) was added finely ground selenium (2.7 mmol) at 20 °C, and the reaction mixture was stirred for 15 min. The unreacted selenium was removed by filtration, and the benzene was evaporated. The residue was recrystallized from pentane. Yield 0.82 g (94%); m.p. 105–106 °C. ^{31}P NMR ($CDCl_3$): δ = 99.4 ($J_{P,Se}$ = 665 Hz) ppm. ^1H NMR ($CDCl_3$): δ = 1.25 (d, $J_{P,H}$ = 6.8 Hz, 6 H, CH_3), 1.26 (d, $J_{P,H}$ = 15.6 Hz, 18 H, CH_3), 1.28 (d, $J_{P,H}$ = 6.8 Hz, 6 H, CH_3), 3.69 (m, 1 H, CH), 4.17 (m, 1 H, CH), 8.11 (d, $J_{P,H}$ = 26.8 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.1 (s, CH_3), 23.0 (s, CH_3), 27.7 [s, $(CH_3)_3$], 38.6 (d, $J_{C,P}$ = 54 Hz, C), 46.7 (s, CH), 50.2 (s, CH), 161.4 (s, CH) ppm. $C_{15}H_{33}N_2PSe$ (351.37): calcd. C 51.27, H 9.47, N 7.97, P 8.81; found C 51.38, H 9.21, N 8.04, P 8.52.

Di-*tert*-butyl{[(diisopropylamino)methylene]amino}(methylselenyl)-phosphonium Trifluoromethanesulfonate (10): To a solution of **8** (2.5 mmol) in DCM (5 mL) at –78 °C was added a solution of methyl trifluoromethanesulfonate (2.5 mmol) in DCM (5 mL) with stirring. After 15 min, the temperature was increased to 20 °C, and the solvent was evaporated. The remaining solid was recrystallized from THF (–20 °C). Yield 1.21 g (94%); m.p. 87–88 °C, white crystals. ^{31}P NMR (CD_3CN): δ = 95.3 ($J_{P,Se}$ = 480 Hz) ppm. ^1H NMR ($CDCl_3$): δ = 1.24 (d, $J_{H,H}$ = 7.8 Hz, 3 H, CH_3Se), 1.31 (d, $J_{P,H}$ = 6.6 Hz, 6 H, CH_3), 1.35 (d, $J_{P,H}$ = 6.6 Hz, 6 H, CH_3), 1.35 (d, $J_{P,H}$ = 17.1 Hz, 18 H, CH_3), 4.02 (m, 1 H, CH), 4.29 (m, 1 H, CH), 7.80 (d, $J_{P,H}$ = 23.4 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 6 (d, $J_{C,P}$ = 5 Hz, CH_3Se), 19.5 (s, CH_3), 22.6 (s, CH_3), 27.0 [s, $(CH_3)_3$], 41.5 (d, $J_{C,P}$ = 47 Hz, C), 48.5 (s, CH), 52.2 (s, CH), 160.0 (s, CH) ppm. MS: *m*/*z* = 366 [M – $CF_3SO_3^-$]$^+$. $C_{17}H_{36}F_3N_2O_3PSSe$ (515.47): calcd. N 5.43, P 6.01; found N 5.63, P 6.38.

***N*,*N*-Diisopropyl-*N′*-(di-*tert*-butylphosphoroselenoyl)formamidine Trifluoromethanesulfonate (11):** To a solution of **8** (2.5 mmol) in DCM (5 mL) at –78 °C was added a solution of trifluoromethanesulfonic acid (2.5 mmol) in DCM (25 mL) with stirring. After 15 min, the temperature was increased to 20 °C and the mixture stirred for 10 min. The solvent was evaporated. The remaining transparent solid was washed with diethyl ether (3× 5 mL) and dried. Yield 1.13 g (90%); m.p. 168–169 °C, white crystals. ^{31}P NMR ($CDCl_3$): δ = 125 ($J_{P,Se}$ = 800 Hz) ppm. ^1H NMR ($CDCl_3$): δ = 1.37 (d, $J_{H,H}$ = 6.9 Hz, 6 H, CH_3), 1.43 (d, $J_{H,H}$ = 6.9 Hz, 6 H, CH_3), 1.43 (d, $J_{P,H}$ = 17.7 Hz, 18 H, CH_3), 4.0 (m, 1 H, CH), 5.04 (m, 1 H, CH), 9.06 (dd, $J_{P,H}$ = 13.2 Hz, $J_{H,H}$ = 9.6 Hz, 1 H, CH), 9.48 (m, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 19.5 (s, CH_3), 24.3 (s, CH_3), 27.4 [s, $(CH_3)_3$], 40.9 (d, $J_{C,P}$ = 38 Hz, C), 50.5 (s, CH), 53.1 (s, CH), 158.2 (d, $J_{C,P}$ = 10 Hz, CH) ppm. $C_{16}H_{34}F_3N_2O_3PSSe$ (501.44): calcd. N 5.59, P 6.18; found N 5.73, P 6.01.

General Procedure for the Synthesis of 13a,b: To a suspension of **1b** (5 mmol) in DCM (25 mL) at –20 °C, a solution of (alkylamino)-phosphane **12** (10 mmol) in DCM (10 mL) was added with stirring. The solution turned brown. The temperature was increased to 20 °C, and the mixture was stirred for 30 min, during which time the color faded. The solvent was evaporated in vacuo until the weight of the residue remained constant. The residue was washed with diethyl ether (3× 20 mL) to remove iPr_2NCHO and dried in vacuo. Then, it was dissolved in THF (25 mL), and NaH (60% in oil, 5 mmol) was added portionwise. When the evolution of hydrogen had ceased, the solvent was evaporated in vacuo. To the residue, DCM (25 mL) was added, and the solid was collected by filtration and washed with DCM. The filtrate was concentrated to dryness, and the residue was washed with diethyl ether (3× 10 mL) to extract (alkylamino)phosphane (90–95%). The residue was dried in vacuo (0.05 Torr) and recrystallized from THF at –10 °C.

{[(Di-*tert*-butylphosphanyl)(methyl)amino]methylene}diisopropylammonium Trifluoromethanesulfonate (13a): ^{31}P NMR (CD_3CN): δ

= 116.9 (br. s), 140.3 (br. s), 150.5 (br. s), integral ratio 1:1.3:4.3. ^{1}H NMR (CD_3CN): δ = 1.33 (d, $J_{P,H}$ = 13.2 Hz, 18 H, CH_3), 1.36 (d, $J_{H,H}$ = 6.3 Hz, 12 H, CH_3), 3.55 (s, 3 H, CH_3), 4.00 (m, 1 H, CH), 4.5–5.5 (m, 1 H, CH), 7.46 (s), 7.90 (d, $J_{H,H}$ = 6.3 Hz, 1 H, CH) ppm. ^{13}C NMR (CD_3CN): δ = 19.5 (br. s, CH_3), 20.0 (br. s, CH_3), 28.4 [d, $J_{C,P}$ = 16 Hz, $C(CH_3)_3$], 35.6 (d, $J_{C,P}$ = 33 Hz, C), 50.4 (s, CH_3N), 52.3 (br. s, CH), 160.5 (br. s, CH) ppm. MS: *m*/*z* = 394 $[M]^+$. $C_{17}H_{36}F_3N_2O_3PS$ (436.51): calcd. C 46.78, H 8.31, N 6.42, P 7.10; found C 46.34, H 8.11, N 6.26, P 7.42. Yield 2.11 g, 97%; m.p. 133–136 °C (THF, white crystals).

{[(Di-*tert*-butylphosphanyl)(isopropyl)amino]methylene}diisopropylammonium Trifluoromethanesulfonate (13b): ^{31}P NMR (CD_3CN): δ = 118.5 (br. s), 96.0 (br. s) ppm; integral ratio 1:0.6. ^{1}H NMR (CD_3CN): δ = 1.31 (d, $J_{P,H}$ = 13 Hz), 1.33 (d, $J_{H,H}$ = 6.5 Hz, 12 H, CH_3), 1.39 (d, $J_{P,H}$ = 13.5 Hz, 18 H, CH_3), 1.41 (d, J = 6.5 Hz), 1.45 (d, J = 6.5 Hz), 1.52 (d, J = 6.5 Hz, 18 H, CH_3), 4.07 (m, 1 H, CH), 4.09 (m, 1 H, CH), 4.27 (m), 4.41 (m), 5.88 (m, 3 H, CH), 7.57 (s), 7.74 (d, $J_{H,H}$ = 12.0 Hz, 1 H, CH) ppm. ^{13}C NMR (CD_3CN): δ = 18.2 (s, CH_3), 19.5 (s, CH_3), 23.0 [d, $J_{C,P}$ = 13.0 Hz, $C(CH_3)_3$], 23.2 (s, CH_3), 23.9 (s, CH_3), 28.9 (d, $J_{C,P}$ = 18 Hz, CH_3), 29.4 (d, $J_{C,P}$ = 16 Hz, CH_3), 35.5 (d, $J_{C,P}$ = 35 Hz, C), 36.5 (d, $J_{C,P}$ = 36 Hz, C), 54.3 (s, CH), 54.6 (s, CH), 54.8 (s, CH), 55.8 (d, $J_{C,P}$ = 11 Hz, CH), 58.3 (d, $J_{C,P}$ = 5 Hz, CH), 158.7 (d, $J_{C,P}$ = 10 Hz, CH), 159.1 (d, $J_{C,P}$ = 9 Hz, CH) ppm. MS: *m*/*z* = 315 $[M]^+$. $C_{19}H_{40}F_3N_2O_3PS$ (464.56): calcd. C 49.12, H 8.68, N 6.03, P 6.67; found C 48.87, H 8.92, N 5.74, P 6.99. Yield 2.2 g, 95%, m.p. 115–117 °C (white crystals, THF).

General Procedure for the Synthesis of 15a,b, 18a–c, and 21a–d: Bromodi(*tert*-butyl)phosphane [prepared from di(*tert*-butyl)chlorophosphane and bromotrimethylsilane, 1 equiv.], the corresponding alkyl(aryl)amine (1.2 equiv.), and triethylamine (1.5 equiv.) were heated to reflux in pyridine for 1–2 h (15 h for adamantylamine) until the bromophosphane (δ = 150–153 ppm) was fully consumed as judged by ^{31}P NMR spectroscopy. The solution was cooled to room temperature,* the pyridine was evaporated in vacuo, and the residue was distilled in vacuo (0.05 Torr). *For the synthesis of selenides: To the reaction mixture, selenium (1.1 equiv.) was added, and the mixture was stirred at room temperature for 1.5 h. The excess selenium was removed by filtration, the pyridine was evaporated, and the target selenides were distilled in vacuo (0.05 Torr).

Di-*tert*-butyl(*p*-tolylamino)phosphane (15b): ^{31}P NMR ($CDCl_3$): δ = 59.8 ppm. ^{1}H NMR ($CDCl_3$): δ = 1.14 (d, $J_{P,H}$ = 11.7 Hz, 18 H, CH_3), 2.25 (s, CH_3), 3.89 (d, $J_{P,H}$ = 10.5 Hz, 1 H, NH), 6.81 (dd, $J_{H,H}$ = 8.7 Hz, J = 2.4 Hz, 2 H, CH), 6.98 (d, $J_{H,H}$ = 8.4 Hz, 2 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.4 (s, CH_3), 28.2 (d, $J_{C,P}$ = 15 Hz, CH_3), 34.2 (d, $J_{C,P}$ = 19 Hz, C), 115.9 (d, $J_{C,P}$ = 11 Hz, CH), 127.3 (s, C), 129.6 (s, CH), 146.9 (d, $J_{C,P}$ = 16 Hz, C) ppm. Yield 96%; b.p. 105–110 °C/0.05 Torr.

General Procedure for the Synthesis of 16a,b: To a solution of **1a** (2.5 mmol) in acetonitrile (40 mL) at –10 °C, a solution of **15** (5 mmol) in acetonitrile (30 mL) was added dropwise with stirring for 15 min. The reaction mixture was stirred at –10 °C for 1 h, the temperature was increased to 20 °C (the reaction mixture turned brown), and the mixture was stirred overnight. The reaction mixture turned light yellow. Triethylamine (3 mmol) was added to the reaction mixture. The solvent was evaporated until the weight was constant. Compound **15** was extracted from the solid residue with hexane (3× 30 mL). Yield: **16a**: 5.1 g (86%); **16b**: 5.65 g (90%). The remaining residue was dissolved in DCM (20 mL), and the resulting solution was washed with water (3× 20 mL). The organic layer was separated, and the solvent was evaporated until the weight was constant. The residue was recrystallized from THF.

2,2-Di-*tert*-butyl-3-(dimethylamino)-2,3-dihydro-1*H*-benzo[*d*][1,2]-azaphosphol-2-ium Trifluoromethanesulfonate (16a): White solid, yield 8.84 g (80%); m.p. 166–167 °C. ^{31}P NMR (CD_3CN): δ = 78.4 ppm. ^{1}H NMR (CD_3CN): δ = 1.48 (d, $J_{P,H}$ = 15 Hz, 18 H, CH_3), 2.45 (s, 6 H, CH_3), 5.49 (s, 1 H, CH), 7.03 (t, $J_{H,H}$ = 7.5 Hz, 1 H, CH), 7.09 (d, 1 H, CH), 7.35 (m, 2 H, CH), 7.53 (d, J = 10.5 Hz, 1 H, NH) ppm. ^{13}C NMR (CD_3CN): δ = 25.7 (s, CH_3), 37.5 [d, $J_{C,P}$ = 33 Hz, $C(CH_3)_3$], 43.5 (d, $J_{C,P}$ = 4 Hz, CH_3N), 68.4 (d, $J_{C,P}$ = 56 Hz, CH), 113.6 (d, $J_{C,P}$ = 9 Hz, CH), 121.2 (s, CH), 122.7 (d, $J_{C,P}$ = 6 Hz, *i*-C), 127.9 (d, $J_{C,P}$ = 14 Hz, CH), 130.9 (s, CH), 145.0 (d, $J_{C,P}$ = 8 Hz, C) ppm. MS: *m*/*z* = 293 $[M]^+$. $C_{18}H_{30}F_3N_2O_3PS$ (442.47): calcd. C 48.86, H 6.83, N 6.33, P 7.00; found C 49.14, H 6.76, N 6.54, P 6.68.

2,2-Di-*tert*-butyl-3-(dimethylamino)-5-methyl-2,3-dihydro-1*H*-benzo-[*d*][1,2]azaphosphol-2-ium Trifluoromethanesulfonate (16b): White solid, yield 8.55 g (75%); m.p. 130–132 °C. ^{31}P NMR (CD_3CN): δ = 79.1 ppm. ^{1}H NMR (CD_3CN): δ = 1.44 (d, $J_{P,H}$ = 15.9 Hz, 18 H, CH_3), 2.29 (s, 3 H, CH_3), 2.41 (d, $J_{P,H}$ = 1.8 Hz, 6 H, CH_3), 5.41 (s, 1 H, CH), 6.95 (t, $J_{H,H}$ = 8.7 Hz, 1 H, CH), 7.13 (m, 2 H, CH), 7.42 (d, $J_{P,H}$ = 11.4 Hz, 1 H, NH) ppm. ^{13}C NMR (CD_3CN): δ = 19.9 (s, CH_3), 25.7 (s, CH_3), 37.4 [d, $J_{C,P}$ = 32 Hz, $C(CH_3)_3$], 43.5 (d, $J_{C,P}$ = 4 Hz, CH_3N), 68.4 (d, $J_{C,P}$ = 58 Hz, CH), 113.3 (d, $J_{C,P}$ = 5 Hz, CH), 122.8 (d, $J_{C,P}$ = 11 Hz, *i*-C), 130.8 (s, C), 131.4 (s, CH), 142.7 (d, $J_{C,P}$ = 8 Hz, C) ppm. $C_{19}H_{32}F_3N_2O_3PS$ (456.50): calcd. C 49.99, H 7.07, N 6.14, P 6.78; found C 50.17, H 6.81, N 6.31, P 6.97.

***P*,*P*-Di-*tert*-butyl-*N*-phenylphosphinoselenoic Amide (18a):** ^{31}P NMR ($CDCl_3$): δ = 95.4 ($J_{P,Se}$ = 763 Hz) ppm. ^{1}H NMR ($CDCl_3$): δ = 1.44 (d, $J_{P,H}$ = 15.9 Hz, 18 H, CH_3), 4.39 (br. s, 1 H, NH), 7.0 (t, $J_{H,H}$ = 7.2 Hz, 1 H, CH), 7.24 (t, $J_{H,H}$ = 8.1 Hz, 2 H, CH), 7.39 (t, $J_{H,H}$ = 8.4 Hz, 2 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 27.9 (d, $J_{C,P}$ = 3 Hz, CH_3), 41.2 (d, $J_{C,P}$ = 44 Hz, C), 121.9 (d, $J_{C,P}$ = 4 Hz, CH), 122.6 (s, CH), 128.6 (s, CH), 142.0 (d, $J_{C,P}$ = 4 Hz, C) ppm. MS: *m*/*z* = 317 $[M]^+$. $C_{14}H_{24}NPSe$ (316.28): calcd. C 53.17, H 7.65, N 4.43; found C 53.42, H 7.44, N 4.12. Yield: 90%; b.p. 180–183 °C/0.05 Torr, m.p. 153–154 °C.

***P*,*P*-Di-*tert*-butyl-*N*-(4-methylphenyl)phosphinoselenoic Amide (18b):** ^{31}P NMR ($CDCl_3$): δ = 96.1 ($J_{P,Se}$ = 831 Hz) ppm. ^{1}H NMR ($CDCl_3$): δ = 1.42 (d, $J_{P,H}$ = 15.9 Hz, 18 H, CH_3), 2.27 (s, 3 H, CH_3), 4.28 (br. s, 1 H, NH), 7.03 (d, $J_{P,H}$ = 8.4 Hz, 2 H, CH), 7.25 (d, $J_{H,H}$ = 8.4 Hz, 2 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.7 (s, CH_3), 28.0 (s, CH_3), 41.1 (d, $J_{C,P}$ = 45 Hz, C), 122.5 (d, $J_{C,P}$ = 3 Hz, CH), 132.3 (s, C), 139.1 (d, $J_{C,P}$ = 4 Hz, CH) ppm. MS: *m*/*z* = 331 $[M]^+$. $C_{15}H_{26}NPSe$ (330.31): calcd. C 54.54, H 7.93, N 4.24; found C 54.21, H 8.17, N 4.64. Yield: 93%; b.p. 180–183 °C/0.05 Torr, m.p. 83–84 °C.

***P*,*P*-Di-*tert*-butyl-*N*-(4-methoxyphenyl)phosphinoselenoic Amide (18c):** ^{31}P NMR ($CDCl_3$): δ = 95.7 ppm. ^{1}H NMR ($CDCl_3$): δ = 1.40 (d, $J_{P,H}$ = 15.9 Hz, 18 H, CH_3), 3.74 (s, CH_3), 4.20 (d, $J_{P,H}$ = 5.4 Hz, 1 H, NH), 6.77 (d, $J_{H,H}$ = 8.7 Hz, 2 H, CH), 7.27 (d, $J_{H,H}$ = 8.7 Hz, 2 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 28.0 (s, CH_3), 40.9 (d, $J_{C,P}$ = 44 Hz, CH_3), 55.5 (s, CH_3), 113.8 (s, C), 125.0 (d, $J_{C,P}$ = 4 Hz, CH), 134.4 (d, $J_{C,P}$ = 4 Hz, C), 155.9 (s, CH) ppm. $C_{15}H_{26}NOPSe$ (346.31): calcd. C 52.02, H 7.57, N 4.04; found C 51.94, H 7.84, N 4.32. Yield: 98%; b.p. 190–192 °C/0.05 Torr, m.p. 133–134 °C.

General Procedure for the Synthesis of 19a–c: To **1b** (5 mmol) at 0 °C was added a solution of **18** (5 mmol) in DMC (30 mL). The temperature was increased to 20 °C over 15 min, and the reaction mixture was stirred for 3 h. The solvent was removed under reduced pressure. The residue was washed with diethyl ether (3× 20 mL). The crystalline residue was collected by filtration, washed with

water (3 × 20 mL), dried with P_2O_5, and then washed with a small amount of THF.

{[(Di-*tert*-butylphosphoroselenoyl)(phenyl)amino]methylene}-diisopropylammonium Trifluoromethanesulfonate (19a): ^{31}P NMR (CD_3CN): δ = 145.3 ($J_{P,Se}$ = 789 Hz) ppm. ^{1}H NMR (CD_3CN): δ = 0.96 (d, $J_{H,H}$ = 6.5 Hz, 6 H, CH_3), 1.50 (d, $J_{H,H}$ = 6.5 Hz, 6 H, CH_3), 1.52 (d, $J_{P,H}$ = 17.5 Hz, 18 H, CH_3), 3.48 (m, 1 H, CH), 4.13 (m, 1 H, CH), 7.62 (m, 5 H, CH), 9.28 (br. s, 1 H, CH) ppm. ^{13}C NMR (CD_3CN): δ = 18.0 (s, CH_3), 23.7 (s, CH_3), 28.5 (s, CH_3), 44.6 [d, $J_{C,P}$ = 28 Hz, $C(CH_3)_3$], 52.8 (s, CH), 53.0 (s, CH), 129.4 (s, CH), 130.5 (s, CH), 131.3 (s, CH), 138.1 (s, C), 158.2 (d, $J_{C,P}$ = 13 Hz, CH) ppm. MS: m/z = 428 $[M]^+$. $C_{22}H_{38}F_3N_2O_3PSSe$ (577.54): calcd. C 45.75, H 6.63, N 4.85, P 5.36; found C 46.11, H 6.81, N 4.51, P 5.72. Yield 2.8 g, 91%; m.p. 168–169 °C.

{[(Di-*tert*-butylphosphoroselenoyl)(4-methylphenyl)amino]methylene}diisopropylammonium Trifluoromethanesulfonate (19b): ^{31}P NMR (CD_3CN): δ = 145.4 ($J_{P,Se}$ = 816 Hz) ppm. ^{1}H NMR (CD_3CN): δ = 0.97 (d, $J_{H,H}$ = 7 Hz, 6 H, CH_3), 1.49 (d, $J_{H,H}$ = 7 Hz, 6 H, CH_3), 1.50 (d, $J_{P,H}$ = 17 Hz, 18 H, CH_3), 2.45 (s, 3 H, CH_3), 3.45 (m, 1 H, CH), 4.08 (m, 1 H, CH), 7.43 (d, $J_{H,H}$ = 8 Hz, 2 H, CH), 7.48 (d, $J_{H,H}$ = 8 Hz, 2 H, CH), 9.28 (br. s, 1 H, CH) ppm. ^{13}C NMR (CD_3CN): δ = 18.01 (s, CH_3), 20.3 (s, CH_3Ar), 23.7 (s, CH_3), 28.5 (s, CH_3), 44.4 [d, $J_{C,P}$ = 29 Hz, $C(CH_3)_3$], 52.5 (s, CH), 52.9 (s, CH), 128.9 (s, CH), 131.1 (s, CH), 135.2 (s, CH), 142.4 (s, C), 158.2 (s, CH) ppm. MS: m/z = 442 $[M]^+$. $C_{23}H_{40}F_3N_2O_3PSSe$ (591.57): calcd. C 46.70, H 6.82, N 4.74, P 5.24; found C 46.49, H 6.53, N 4.99, P 5.61. Yield 2.75 g, 93%; m.p. 163–164 °C.

{[(Di-*tert*-butylphosphoroselenoyl)(4-methoxyphenyl)amino]methylene}diisopropylammonium Trifluoromethanesulfonate (19c): ^{31}P NMR ($CDCl_3$): δ = 145.1 ($J_{P,Se}$ = 816 Hz) ppm. ^{1}H NMR ($CDCl_3$): δ = 0.99 (d, $J_{H,H}$ = 6.6 Hz, 6 H, CH_3), 1.44 (d, $J_{P,H}$ = 17.5 Hz, 18 H, CH_3), 1.49 (d, $J_{H,H}$ = 6.6 Hz, 6 H, CH_3), 3.60 (m, 1 H, CH), 3.86 (s, CH_3), 4.04 (m, 1 H, CH), 7.12 (d, $J_{H,H}$ = 9 Hz, 2 H, CH), 7.47 (d, $J_{H,H}$ = 9 Hz, 2 H, CH), 9.67 (d, $J_{H,H}$ = 7.5 Hz, 1 H, CH) ppm. ^{13}C NMR (CD_3CN): δ = 18.1 (s, CH_3), 23.7 (s, CH_3), 28.5 (s, CH_3), 44.3 [d, $J_{C,P}$ = 28 Hz, $C(CH_3)_3$], 52.4 (s, CH), 52.9 (s, CH), 55.7 (s, CH_3O), 115.6 (s, CH), 129.8 (s, C), 130.4 (s, CH), 158.4 (d, $J_{H,H}$ = 14 Hz, CH), 161.5 (s, C) ppm. MS: m/z = 458 $[M]^+$. $C_{23}H_{40}F_3N_2O_4PSSe$ (607.57): calcd. C 45.47, H 6.64, N 4.61, P 5.10; found C 45.72, H 6.89, N 4.39, P 5.48. Yield 2.88 g, 95%; m.p. 129–130 °C.

General Procedure for the Synthesis of 20a–c: To a solution of **19** (5 mmol) in DCM (15 mL) at 20 °C, hexamethylphosphorous triamide was added (5.5 mmol) dropwise with stirring. After 30 min, the solvent was evaporated to dryness. Dry diethyl ether (40 mL) was added to the residue. The flask was shaken until a crystalline solid had formed. The solid was collected by filtration, washed with diethyl ether, and dried to constant weight in vacuo (0.05 Torr). If necessary, these compounds can be recrystallized from dry THF.

{[(Di-*tert*-butylphosphanyl)(phenyl)amino]methylene}diisopropylammonium Trifluoromethanesulfonate (20a): ^{31}P NMR ($CDCl_3$): δ = 136.6 ppm. ^{1}H NMR (CD_3CN): δ = 0.98 (d, $J_{H,H}$ = 6.6 Hz, 6 H, CH_3), 1.35 (d, $J_{P,H}$ = 13.2 Hz, 18 H, CH_3), 1.47 (d, $J_{H,H}$ = 6.6 Hz, 6 H, CH_3), 3.65 (m, 1 H, CH), 4.05 (m, 1 H, CH), 7.42 (d, $J_{H,H}$ = 7.8 Hz, 2 H, CH), 7.51 (m, 3 H, CH), 7.81 (br. s, 1 H, CH) ppm. ^{13}C NMR (CD_3CN): δ = 17.7 (s, CH_3), 23.2 (s, CH_3), 28.5 [d, $J_{C,P}$ = 16 Hz, $C(CH_3)_3$], 36.4 (d, $J_{C,P}$ = 38 Hz, C), 50.8 (s, CH), 51.9 (s, CH), 126.2 (br. s, CH), 129.2 (br. s, CH), 130.4 (s, CH), 144.5 (br. s, C), 155.6 (br. s, CH) ppm. $C_{22}H_{38}F_3N_2O_3PS$ (498.58): calcd. C 53.00, H 7.68, N 5.62, P 6.21; found C 53.13, H 7.61, N 5.71, P 6.49. Yield 2.46 g, 99%; m.p. 171–172 °C (white crystals).

{[(Di-*tert*-butylphosphanyl)(4-methylphenyl)amino]methylene}diisopropylammonium Trifluoromethanesulfonate (20b): ^{31}P NMR (CD_3CN): δ = 137.5 ppm. ^{1}H NMR (CD_3CN): δ = 0.98 (d, $J_{H,H}$ = 6.6 Hz, 6 H, CH_3), 1.34 (d, $J_{P,H}$ = 12.9 Hz, 18 H, CH_3), 1.46 (d, $J_{H,H}$ = 6.6 Hz, 6 H, CH_3), 2.38 (s, 3 H, CH_3), 3.69 (m, 1 H, CH), 4.04 (m, 1 H, CH), 7.28 (d, $J_{H,H}$ = 7.8 Hz, 2 H, CH), 7.34 (d, $J_{H,H}$ = 8.7 Hz, 2 H, CH), 7.76 (br. s, 1 H, CH) ppm. ^{13}C NMR (CD_3CN): δ = 17.9 (s, CH_3), 20.1 (s, CH_3Ar), 23.3 (s, CH_3), 28.6 [d, $J_{C,P}$ = 16 Hz, $C(CH_3)_3$], 36.5 (d, $J_{C,P}$ = 38 Hz, C), 50.8 (s, CH), 51.8 (s, CH), 126.0 (br. s, CH), 130.9 (s, CH), 139.8 (s, C), 142.0 (br. s, C), 155.7 (br. s, CH) ppm. $C_{23}H_{40}F_3N_2O_3PS$ (512.61): calcd. C 53.89, H 7.87, N 5.46, P 6.04; found C 54.11, H 7.91, N 5.21, P 6.51. Yield 2.51 g, 98%; m.p. 163–164 °C.

{[(Di-*tert*-butylphosphanyl)(4-methoxyphenyl)amino]methylene}diisopropylammonium Trifluoromethanesulfonate (20c): ^{31}P NMR (CD_3CN): δ = 137.9 ppm. ^{1}H NMR (CD_3CN): δ = 1.00 (d, $J_{H,H}$ = 6.6 Hz, 6 H, CH_3), 1.34 (d, $J_{P,H}$ = 12.9 Hz, 18 H, CH_3), 1.46 (d, $J_{H,H}$ = 6.6 Hz, 6 H, CH_3), 3.72 (m, 1 H, CH), 3.86 (s, 3 H, CH_3), 4.04 (m, 1 H, CH), 7.03 (d, $J_{H,H}$ = 9 Hz, 2 H, CH), 7.33 (d, $J_{H,H}$ = 9 Hz, 2 H, CH), 7.75 (br. s, 1 H, CH) ppm. ^{13}C NMR (CD_3CN): δ = 18.0 (s, CH_3), 23.3 (s, CH_3), 28.6 (d, $J_{C,P}$ = 16 Hz, CH_3), 36.4 [d, $J_{C,P}$ = 38 Hz, $C(CH_3)_3$], 50.7 (s, CH), 51.7 (s, CH), 55.6 (s, CH_3O), 115.4 (s, CH), 127.4 (br. s, CH), 137.0 (br. s, C), 155.6 (br. s, CH), 159.9 (br. s, C) ppm. $C_{23}H_{40}F_3N_2O_4PS$ (528.61): calcd. C 52.26, H 7.63, N 5.30, P 5.86; found C 52.41, H 7.91, N 5.02, P 6.21. Yield 2.59 g (98%); m.p. 148–149 °C (white crystals).

***P,P*-Di-*tert*-butyl-*N*-methylphosphinoselenoic Amide (21a):** ^{31}P NMR ($CDCl_3$): δ = 103.5 ($J_{P,Se}$ = 739 Hz) ppm. ^{1}H NMR ($CDCl_3$): δ = 1.33 (d, $J_{P,H}$ = 16 Hz, 18 H, CH_3), 1.85 (br. s, 1 H, NH), 2.79 (d, $J_{P,H}$ = 12 Hz, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 27.8 (d, $J_{C,P}$ = 1 Hz, CH_3), 31.0 (d, $J_{C,P}$ = 3 Hz, CH_3), 40.2 (d, $J_{C,P}$ = 47 Hz, C) ppm. MS: m/z = 255 $[M]^+$. $C_9H_{22}NPSe$ (254.21): calcd. C 42.52, H 8.72, N 5.51; found C 42.31, H 9.03, N 5.40. Yield 91%; b.p. 120–122 °C/0.05 Torr, m.p. 114–115 °C (white crystals).

***N,P,P*-Tri-*tert*-butylphosphinoselenoic Amide (21c):** ^{31}P NMR ($CDCl_3$): δ = 89.8 ($J_{P,Se}$ = 748 Hz) ppm. ^{1}H NMR ($CDCl_3$): δ = 1.29 (d, $J_{P,H}$ = 15.6 Hz, 18 H, CH_3), 1.41 (s, 9 H, CH_3), 1.73 (br. s, 1 H, NH) ppm. ^{13}C NMR ($CDCl_3$): δ = 27.9 (d, $J_{C,P}$ = 1 Hz, CH_3), 32.9 (d, $J_{C,P}$ = 3 Hz, CH_3), 40.1 (d, $J_{C,P}$ = 47 Hz, C), 54.2 (d, $J_{C,P}$ = 4 Hz, C) ppm. $C_9H_{22}NPSe$ (254.21): calcd. C 48.64, H 9.53, N 4.73; found C 48.81, H 9.71, N 4.41. Yield 98%; b.p. 125–127 °C/0.05 Torr, m.p. 102–104 °C (white crystals).

***N*-Adamantyl-*P,P*-di-*tert*-butylphosphinoselenoic Amide (21d):** ^{31}P NMR ($CDCl_3$): δ = 85.6 ($J_{P,Se}$ = 733 Hz) ppm. ^{1}H NMR ($CDCl_3$): δ = 1.34 (d, $J_{P,H}$ = 15.5 Hz, 18 H, CH_3), 1.61 (br. s, 1 H, NH), 1.64 (m, 6 H, CH_2), 2.07 (m, 3 H, CH), 2.13 (m, 6 H, CH_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 27.9 (d, $J_{C,P}$ = 3 Hz, CH_3), 30.3 (s, CH), 36.3 (s, CH_2), 40.0 (d, $J_{C,P}$ = 39 Hz, C), 45.9 (d, $J_{C,P}$ = 4 Hz, CH_2), 54.7 (d, $J_{C,P}$ = 5 Hz, C) ppm. $C_{18}H_{34}NPSe$ (374.41): calcd. C 57.74, H 9.15, N 3.74; found C 57.41, H 8.92, N 3.61. Yield 92%; b.p 180–182 °C/0.05 Torr, m.p. 168–169 °C (white crystals).

4,4-Di-*tert*-butyl-2,8-dimethyl-7-(propan-2-yl)-5-selena-3,7-diaza-4-phosphanon-6-ene-4,7-diium Bis(trifluoromethanesulfonate) (22b): To a suspension of **1b** (10 mmol) in DCM (20 mL) at 20 °C, a solution of **21b** (10 mmol) in DCM (20 mL) was added with stirring. After 2 h, the solution was cooled to 0 °C and stirred for 30 min. The precipitated solid was collected by filtration, washed twice with DCM, dried, and recrystallized from DCM. Yield 2.82 g, 52%; m.p. 135–137 °C (white crystals). ^{31}P NMR (CD_3CN): δ = 108.2 ($J_{P,Se}$ = 354 Hz) ppm. ^{1}H NMR (CD_3CN): δ = 1.41 (d, $J_{H,H}$ = 6.0 Hz, 6 H, CH_3), 1.51 (d, $J_{H,H}$ = 6.5 Hz, 6 H, CH_3), 1.56 (d, $J_{H,H}$ = 6.5 Hz, 6 H, CH_3), 1.63 (d, $J_{P,H}$ = 19.5 Hz, 18 H, CH_3), 4.01 (m,

1 H, CH), 4.61 (m, 2 H, CH), 5.78 (m, 1 H, NH), 9.44 (d, $J_{H,H}$ = 6.5 Hz, 1 H, CH) ppm. ^{13}C NMR (CD_3CN): δ = 19.1 (s, CH_3), 23.1 (s, CH_3), 24.3 (d, $J_{C,P}$ = 5 Hz, CH_3), 27.9 (s, CH_3), 44.6 [d, $J_{C,P}$ = 32 Hz, $C(CH_3)_3$], 50.8 (d, $J_{C,P}$ = 9 Hz, CH), 62.1 (s, CH), 66.2 (s, CH), 173.5 (s, CH) ppm. $C_{20}H_{41}F_6N_2O_6PS_2Se$ (693.60): calcd. C 34.63, H 5.96, N 4.04; found C 34.24, H 5.65, N 3.89.

General Procedure for the Reaction of 21a–d with Alder's Dimer 1b: To a suspension of **1b** (10 mmol) in DCM (20 mL) at 20 °C, a solution of **21a**–**d** (10 mmol) in DCM (10 mL) was added with stirring. For **21a**, the reaction mixture was stirred for 30 min (**21b**: 72 h), and then the solvent was evaporated to dryness. The residue was extracted with diethyl ether (4× 30 mL) at 30 °C. The undissolved crystalline residue was dried in vacuo. For **21c** and **21d**: After 3 h, iPr$_2$NEt (10 mmol) was added. The solvent was evaporated to dryness. The residue was extracted with hexane (3× 20 mL). The hexane was evaporated, and the residue was subjected to plate chromatography on silica gel (DCM) to give **11**, R_f = 0.6–0.8. Yield: **21c**: 2.21 g (63%); **21d**: 2.77 g, (79%).

{[(Di-*tert*-butylphosphoroselenoyl)(methyl)amino]methylene}-diisopropylammonium Trifluoromethanesulfonate (23a): ^{31}P NMR ($CDCl_3$): δ = 143.3 ($J_{P,Se}$ = 808 Hz) ppm. ^{1}H NMR ($CDCl_3$): δ = 1.37 (d, $J_{H,H}$ = 6.6 Hz, 12 H, CH_3), 1.54 (d, $J_{P,H}$ = 17.4 Hz, 18 H, CH_3), 3.85 (d, $J_{H,H}$ = 6 Hz, 3 H, CH_3), 4.05 (m, 1 H, CH), 5.04 (m, 1 H, CH), 9.51 (d, $J_{H,H}$ = 9.9 Hz, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.8 (s, CH_3), 24.6 (s, CH_3), 40.3 (s, NCH_3), 43.6 (d, $J_{C,P}$ = 30 Hz, C), 52.7 (s, CH), 53.3 (s, CH), 160.9 (d, $J_{C,P}$ = 15 Hz, CH) ppm. $C_{17}H_{36}F_3N_2O_3PSSe$ (515.47): calcd. C 39.61, H 7.04, N 5.43, P 6.01; found C 39.21, H 6.79, N 5.51, P 5.79. Yield 3.81 g (74%); m.p. 197–198 °C, white crystals.

{[(Di-*tert*-butylphosphoroselenoyl)(isopropyl)amino]methylene}-diisopropylammonium Trifluoromethanesulfonate (23b): ^{31}P NMR (CD_3CN): δ 133.5 (br. s) ppm. ^{1}H NMR (CD_3CN): δ = 1.45 (d, $J_{H,H}$ = 6.6 Hz, 6 H, CH_3), 1.50 (d, $J_{H,H}$ = 6.6 Hz, 6 H, CH_3), 1.57 (d, $J_{P,H}$ = 17.4 Hz, 18 H, CH_3), 4.31 (m, 1 H, CH), 4.66 (m, 1 H, CH), 4.83 (m, 1 H, CH), 8.66 (d, $J_{H,H}$ = 5.7 Hz, 1 H, CH) ppm. ^{13}C NMR (CD_3CN): δ = 19.3 (s, CH_3), 23.1 (s, CH_3), 23.9 (s, CH_3), 29.4 (s, CH_3), 45.2 (d, $J_{C,P}$ = 43 Hz, C), 55.1 (s, CH), 56.4 (s, CH), 56.8 (s, CH), 161.2 (d, $J_{C,P}$ = 10 Hz, CH) ppm. MS: m/z = 394 $[M]^+$. $C_{19}H_{40}F_3N_2O_3PSSe$ (543.52): calcd. C 41.99, H 7.42, N 5.15, P 5.70; found C 42.13, H 7.61, N 5.53, P 5.32. Yield 3.2 g (59%); m.p. 135–136 °C, white crystals.

Supporting Information (see footnote on the first page of this article): Crystallographic data for **3**, **13a**, **13b**, **16**, **19a**, **20a**, **22b**, and **23b** and detailed calculated data for **13**, **19a**, **20a**, **22b**, and **23b**.

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