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Stereoselective free-radical addition of secondary phosphine selenides to aromatic acetylenes

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ABSTRACT

Free-radical addition (AIBN, 65–70 °C, 5–7 h) of secondary phosphine selenides to arylacetylenes proceeds stereoselectively to give anti-Markovnikov adducts of predominantly *Z*-configuration (up to 97%) in 60–80% isolated yields, thus representing a rare example of stereoselective free-radical addition to the triple bond. Microwave irradiation (600 W) of the reactants with the same content of AIBN reduces the reaction time to 8 min though compromises the stereoselectivity. Under UV-initiation the reaction loses its stereoselectivity due to isomerization of the primary *Z*-adducts. In this reaction, a specific facilitating and *Z*-configuration-controlling effect of aromatic substituents at the triple bond has been revealed.

1. Introduction

Stereoselective addition of diverse compounds to substituted acetylenes is a subject of continuous attention of synthetic community [1]. A lot of efforts keep being undertaken to effect the addition as selective as possible. To meet this goal, particularly productive is application of transition metal catalysts [1a–c, f–h]. However, the reliable control of stereoselective addition to the triple bond still remains a synthetic challenge and the investigations in this area are being extended. In numerous publications concerning this important issue, the free-radical addition to the triple bond is still almost neglected, since it is accepted as a common place that such processes are not stereoselective. Among rare exceptions is our recent short communication [2] about stereoselective addition of secondary phosphine sulfides to aryl- and hetarylacetylenes. This finding stimulates us to pay closer attention to the free-radical addition to acetylenes as a prospective source of isomerically pure 1,2-substituted alkenes. Therefore, we have studied the free-radical addition of available [3] secondary phosphine selenides to acetylenes. Apart from addressing the steroselectivity issue which could have an impact on wide circles of organic chemists, we have also followed the straight synthetic goal to develop a short-cut to a novel family of alkenylphosphine selenides. Alkenylphosphine chalcogenides are highly reactive building blocks which interact readily with different nucleophilic (amines [4], thiols [4e], phosphines [5], and carbanion [6] species) and other [7] reactants to afford functional phosphine chalcogenides. The latter are widely applied as hemilabile ligands for the design of advanced catalysts [8], flame retardants [9], extractants of rare earth and transuranic elements [10], precursors and coordinating solvents for the synthesis of conductive nanomaterials [11].

2. Results and discussion

We found that in the presence of azaisobutyronitrile (AIBN) at 65–70 °C (5–7 h, no solvent) secondary phosphine selenides **1–4** added to phenylacetylene **5** (3-fold molar excess) to give anti-Markovnikov adducts **6a-d** of *Z*-configuration predominantly in 60–80% isolated yield (Table 1). The only exclusion was the result obtained for the most bulky phosphine selenide **3** (R = 4-*t*-$BuC_6H_4CH_2CH_2$), when the *Z*-selectivity dropped (*Z*-isomer content in the adduct mixture was 75%), obviously due to steric compression. Despite the remarkable difference in the phosphine selenide **1-4** structure, no noticeable substituents effect on the adduct yield was observed (the yield ranges 70–80%). Only in the case of the compound **4** with 2-pyridylethyl moieties the yield decreased to 60% at a longer reaction time (7 h), that was likely associated with a lower stability of both PH-reagent **4** and adduct **6d**.

The microwave irradiation (600 W) of the reaction mixture (equimolar ratio of the reactants, AIBN, dioxane as a solvent) accelerated the addition dramatically: in 50 s the conversion of the initial phosphine selenide **2** was 60% (NMR ^{31}P), the *Z*-selectivity retaining 90%. At a longer microwave irradiation (8 min), the complete conversion of **2** was reached (the isolated yield of adduct **6b**

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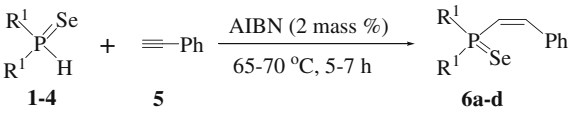
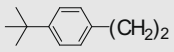
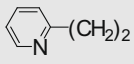
Table 1
Stereoselective addition of secondary phosphine selenides to phenylacetylene[a].



1-4 **5** **6a-d**

Initial phosphine selenide	R^1	Time, h	Adduct **6**	Yield, %		*Z*-isomer content[d], %
				[b]	[c]	
1	Ph	5	**a**	90	75	97
2	$Ph(CH_2)_2$	5	**b**	86	70	91
3		5	**c**	85	80	75
4		7	**d**	75	60	95

[a] All experiments were carried out under argon atmosphere. Molar ratio of reactants **1**–**4**:**5** = 1:3.
[b] Calculated based on ^{31}P NMR spectra of the crude products.
[c] Isolated yield (based on the quantity of phosphine selenide **1-4** charged), conversion of the latter is 100%.
[d] Determined by ^{31}P NMR spectra of the crude products.

was 70%), though the addition selectivity was lost (*Z*:*E* = 52:48), Scheme 1.

It clearly shows that microwave activation facilitates both the addition reaction and the *Z*- to *E*- isomerization. Despite this disadvantage the microwave assistance of the free-radical addition of secondary phosphine selenides to acetylenes can be successfully used when the isomer composition of the adduct is not of primary importance.

The same was true for the UV-initiated addition of secondary phosphine selenides to acetylenes which proved to be almost as effective as that initiated by AIBN (when the adduct yields were concerned). In this case the yields of the adducts ranged from 53% to 80%, while the reaction lasted 4–6 h. However, as expected, UV-irradiation caused the rapid *Z*- to *E*-isomerization of the adducts and hence the stereoselectivity was breached (Table 2).

The easy *Z*- to *E*-isomerization of the adducts under the action of UV-irradiation was illustrated by the photochemical (the same UV-source, 7 h) conversion of *Z*-adduct **6a** (*Z*-isomer content 97%) to the mixture of *Z*- and *E*-isomers in ~1:1 ratio (Scheme 2).

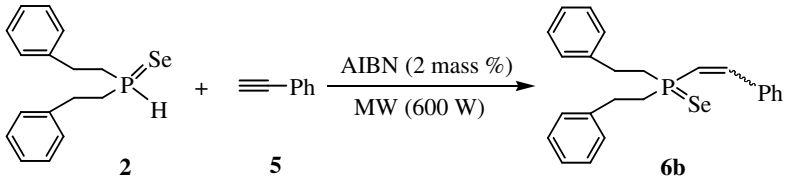
From the comparison of the adduct yields for phenylacetylene (adduct **6a**, yield 88%) and 2-naphtylacetylene (adduct **6e**, yield 60%), it may be concluded that the steric requirements are important for the photochemical version of the addition (Table 2).

However, a key contribution to the substituent effect on this reaction belongs to electronic and specific interaction in the intermediate radical adduct. It follows from the fact that alkynes were proved to be practically inactive in the addition studied. For example, in the case of 1-hexyne and phosphine selenide **2** under the above conditions (AIBN, 65–70 °C) the conversion of **2** was 14% only (^{31}P NMR), though the reaction time was 2.4 times longer (12 h). Another substituted alkyne, 2-propyne-1-ol (phosphine selenide **2**, AIBN, 65–70 °C, 25 h or UV-irradiation, 20 h), turned out to be completely inactive in this addition.

Therefore, it is the aromatic or heteroaromatic substituent at the triple bond that makes the addition both possible and stereoselective.

The strong activation influence of aromatic and heteroaromatic substituents on rate and stereoselectivity of the addition can be rationalized as follows (Scheme 3): the initial radical-adduct **A** is capable of stabilizing by electronic interaction with adjacent aromatic (or heteroaromatic) ring to distribute the radical center over the aromatic system (form **B**). The further through-space spin interaction with the P═Se moiety closes the 6-membered ring radical **C**. Such an intra-molecular single-electron bonding should secure substituents of the adducts formed in the *cis* (*Z*) disposition.

It is pertinent to note that secondary phosphines show low reactivity in the reactions of radical addition to the triple bond. For example, the heating (65–70 °C, 5 h) of bis(2-phenylethyl)phosphine with phenylacetylene in the presence of AIBN gave phosphine **9** in 12% yield, the conversion of initial phosphine being 15% (^{31}P NMR). At the same time we managed to obtain phosphine **9** (as a mixture *Z*:*E* = 80:20) in almost quantitative

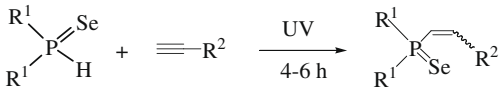


2 **5** **6b**

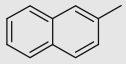
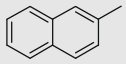
50 sec: conversion of **2** = 60%; **6b**, *Z* : *E* = 90 : 10
8 min: conversion of **2** = 100%; **6b**, *Z* : *E* = 52 : 48

Scheme 1. Reaction of phosphine selenide **2** with phenylacetylene **5** under microwave irradiation.

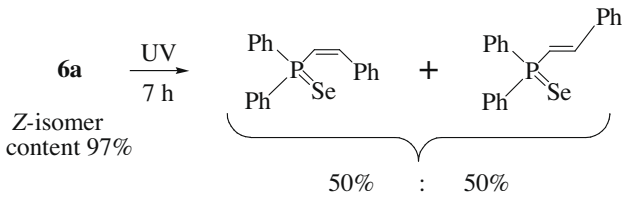
Table 2
Addition of secondary phosphine selenides to acetylenes under UV-initiation[a].



1-3 **5, 7, 8** **6a, c, e-g**

Initial phosphine selenide	Acetylene	R^2	Time, h	Adduct **6**	Yield, %		$Z:E$[d], %
					[b]	[c]	
1	**5**	Ph	4	**a**	88	80	60:40
1	**7**		4	**e**	60	53	60:40
2	**7**		5	**f**	77	74	50:50
2	**8**		6	**g**	65	60	35:65
3	**5**	Ph	4	**c**	68	65	60:40

[a] UV-irradiation (200-W Hg arc lamp), quartz ampoule, solvent – dioxane, argon atmosphere, molar ratio of reactants **1–3**:**5**,**7**,**8** = 1:1.
[b] Calculated based on ^{31}P NMR spectra of the crude products.
[c] Isolated yield (based on the quantity of phosphine selenide **1–3** charged), conversion of the latter was 100%.
[d] Determined by ^{31}P NMR spectra of the crude products.

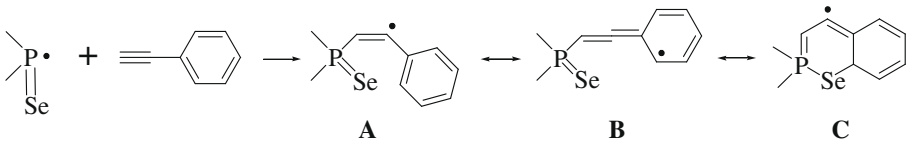


Scheme 2. *Z*- to *E*-isomerization of the adducts under UV-initiation (200-W Hg arc lamp, quartz ampoule, solvent – dioxane).

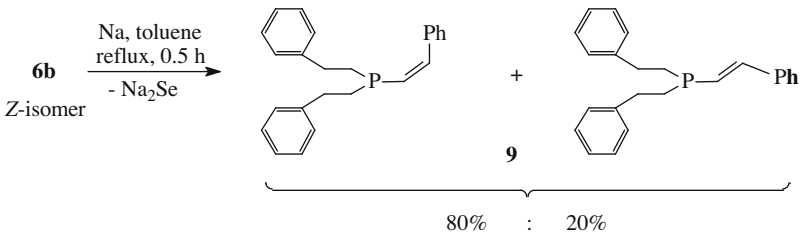
yield by the reduction of *Z*-isomer of the corresponding phosphine selenide **6b** with metal sodium in toluene (reflux, 0.5 h) (Scheme 4).

3. Conclusions

In summary, a facile stereoselective free-radical addition of available[3] secondary phosphine selenides to aromatic and heteroaromatic acetylenes has been found. A specific effect of an aromatic substituent in acetylenes that facilitates the reaction and fixes *Z*-configuration of the adducts has been observed. The results presented contribute to fundamental and synthetic chemistry of



Scheme 3.



Scheme 4.

phosphorus, selenium and acetylenes, particularly to the controlling the addition selectivity to acetylenes. The reaction studied paves a short way to a rare family of isomerically pure alkenes bearing phosphine selenide and aromatic (or heteroaromatic) substituents, potent building blocks for organic and elementoorganic synthesis.

4. Experimental

The ^{1}H, ^{13}C, ^{31}P and ^{77}Se NMR spectra were recorded on a Bruker DPX 400 and Bruker AV-400 spectrometer (400.13, 100.69, 161.98 and 76.31 MHz, respectively) in $CDCl_3$ solutions and referenced to HMDS (^{1}H NMR, ^{13}C NMR), H_3PO_4 (^{31}P NMR) and Me_2Se (^{77}Se NMR). IR spectra were run on a Bruker IFS 25 instrument. GC/MS analyses (EI, 70 eV) were performed on a Hewlett-Packard HP 5971A instrument. All steps of the experiment were carried out in inert atmosphere (argon). Secondary phosphine selenides **1–4** were prepared by the oxidation of corresponding secondary phosphines by elemental selenium in benzene [3a], the initial diphenylphosphine was a commercial product, bis(2-aryl)- or bis(2-hetaryl)ethylphosphines were obtained from red phosphorus and alkene: styrene [3b], 1-(*tert*-butyl)-4-vinylbenzene) [3c] or 2-vinylpyridine [1e].

4.1. Synthesis and characteristics of alkenylphosphine selenides **6a–d** in the presence of AIBN: typical procedure (Table 1)

A mixture of phosphine selenide **1–4** and acetylene **5** (their molar ratio was 1:3) in the presence of 2 mass% AIBN was stirred under an argon atmosphere at 65–70 °C. The reaction was monitored using ^{31}P NMR spectra that showed the disappearance of peaks of the initial secondary phosphine selenide **1–4** at ~2–5 (δ) ppm and the appearance of new peaks at ~20–35 ppm corresponding to tertiary alkenylphosphine selenides **6a–d**. The excess phenylacetylene was then removed under vacuum, the residue was washed twice with small amount of diethyl ether and dried in vacuum to afford alkenylphosphine selenides **6a–d**.

4.1.1. (2-Phenylvinyl)(diphenyl)phosphine selenide (**6a**)

Waxy product, yield 75%, *Z*:*E* = 97:3. Anal. Calc. for $C_{20}H_{17}PSe$: C, 65.40; H, 4.67; P, 8.43; Se, 21.50. Found: C, 65.70; H, 4.38; P, 8.15; Se, 21.78%. IR (film, ν, cm^{-1}): 1656 (C=C), 486 (P=Se). NMR for ***Z*-isomer**: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 6.41 (dd, $^{2}J_{HP}$ = 18.1 Hz, $^{3}J_{HH}$ = 13.5 Hz, 1H, =CHP), 7.00 (m, H_m, H_p, 3H, PhC=), 7.25 (m, H_m, 4H, PhP), 7.27 (m, H_p, 2H, PhP), 7.37 (dd, $^{3}J_{HP}$ = 43.8 Hz, $^{3}J_{HH}$ = 13.5 Hz, 1H, =CHPh), 7.46 (m, H_o, 2H, PhC=), 7.86 (m, H_o, 4H, PhP). ^{13}C NMR (100.69 MHz, $CDCl_3$): δ 122.05 (d, $^{1}J_{CP}$ = 74.1 Hz, =CP), 127.40 (C_m, PhC=), 128.40 (d, $^{3}J_{CP}$ = 12.5 Hz, C_m, PhP), 128.81 (C_p, PhC=), 130.19 (d, $^{4}J_{CP}$ = 1.1 Hz, C_o, PhC=), 131.32 (d, $^{4}J_{CP}$ = 3.0 Hz, C_p, PhP), 131.78 (C_i, $^{1}J_{CP}$ = 72.0 Hz, PhP), 131.80 (d, $^{2}J_{CP}$ = 11.0 Hz, C_o, PhP), 134.30 (d, $^{3}J_{CP}$ = 6.6 Hz, C_i, PhC=), 145.85 (d, $^{2}J_{CP}$ = 2.2 Hz, =*C*Ph). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 20.19 ($^{1}J_{SeP}$ = 719.2 Hz). NMR for ***E*-isomer**: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 6.92 (dd, $^{2}J_{HP}$ = 20.1 Hz, $^{3}J_{HH}$ = 16.4 Hz, 1H, =CHP), 7.35 (m, H_m, H_p, 3H, PhC=), 7.44 (m, H_m, H_p, 6H, PhP), 7.52 (m, H_o, 2H, PhC=), 7.52 (dd, $^{3}J_{HP}$ = 33.9 Hz, $^{3}J_{HH}$ = 16.4 Hz, 1H, =CHPh), 7.80 (m, H_o, 4H, PhP). ^{13}C NMR (100.69 MHz, $CDCl_3$): δ 118.73 (d, $^{1}J_{CP}$ = 78.5 Hz, =CP), 128.08 (C_o, PhC=), 128.30 (C_p, PhC=), 128.40 (C_m, PhP), 128.70 (C_m, PhC=), 130.0 (C_p, PhP), 131.80 (C_o, PhP), 131.90 (C_i, PhP), 134.90 (d, $^{3}J_{CP}$ = 19.8 Hz, C_i, PhC=), 148.94 (d, $^{2}J_{CP}$ = 6.6 Hz, =*C*Ph). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 29.01 ($^{1}J_{SeP}$ = 729.1 Hz).

4.1.2. (2-Phenylvinyl)[bis(2-phenylethyl)]phosphine selenide (**6b**)

Waxy product, yield 70%, *Z*:*E* = 91:9. IR (film, ν, cm^{-1}): 1638 (C=C), 474 (P=Se). Anal. Calc. for $C_{24}H_{25}PSe$: C, 68.08; H, 5.95; P, 7.32; Se, 18.65. Found: C, 67.82; H, 6.01; P, 7.05; Se, 18.94%. ***Z*-isomer**: is colorless solid, mp 84–86 °C (hexane). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.25 (m, 4H, CH_2P), 2.77 (m, 4H, CH_2Ph), 5.98 (dd, $^{2}J_{HP}$ = 18.1 Hz, $^{3}J_{HH}$ = 13.5 Hz, 1H, =CHP), 6.92 (m, H_o, 4H, $PhCH_2$), 7.16 (m, H_p, 2H, $PhCH_2$), 7.21 (m, H_m, 4H, $PhCH_2$), 7.29 (dd, $^{3}J_{HP}$ = 41.0 Hz, $^{3}J_{HH}$ = 13.5 Hz, 1H, =CHPh), 7.36 (m, H_p, 1H, PhC=), 7.42 (m, H_m, 2H, PhC=), 7.82 (m, H_o, 2H, PhC=). ^{13}C NMR (100.69 MHz, $CDCl_3$): δ 29.58 (d, $^{2}J_{CP}$ = 2.3 Hz, CH_2Ph), 33.17 (d, $^{1}J_{CP}$ = 46.2 Hz, CH_2P), 121.57 (d, $^{1}J_{CP}$ = 62.9 Hz, =CP), 126.54 (C_p, $PhCH_2$), 128.25 (C_o, $PhCH_2$), 128.61 (C_m, PhC=), 128.68 (C_m, $PhCH_2$), 129.45 (C_p, PhC=), 129.67 (C_o, PhC=), 135.85 (d, $^{3}J_{CP}$ = 6.5 Hz, C_i, PhC=), 140.48 (d, $^{3}J_{CP}$ = 15.3 Hz, C_i, $PhCH_2$), 145.55 (d, $^{2}J_{CP}$ = 2.7 Hz, =*C*Ph). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 20.71 ($^{1}J_{SeP}$ = 688.3 Hz). NMR for ***E*-isomer**: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.38 (m, 4H, CH_2P), 2.87 (m, 4H, CH_2Ph), 6.31 (dd, $^{2}J_{HP}$ = 21.8 Hz, $^{3}J_{HH}$ = 16.6 Hz, 1H, =CHP), 7.15–7.23 (m, 10H, $PhCH_2$), 7.36 (m, H_m, H_p, 3H, PhC=), 7.45 (m, H_o, 2H, PhC=), 7.59 (dd, $^{3}J_{HP}$ = 23.0 Hz, $^{3}J_{HH}$ = 16.6 Hz, 1H, =CHPh). ^{13}C NMR (100.69 MHz, $CDCl_3$): δ 29.20 (CH_2Ph), 33.30 (d, $^{1}J_{CP}$ = 47.5 Hz, CH_2P), 116.73 (d, $^{1}J_{CP}$ = 70.5 Hz, =CP), 126.40 (C_p, $PhCH_2$), 128.10 (C_o, PhC=), 128.50 (C_o, $PhCH_2$), 128.60 (C_m, $PhCH_2$), 128.97 (C_m, PhC=), 130.20 (C_p, PhC=), 134.74 (d, $^{3}J_{CP}$ = 19.6 Hz, C_i, PhC=), 140.68 (d, $^{3}J_{CP}$ = 15.4 Hz, C_i, $PhCH_2$), 151.10 (d, $^{2}J_{CP}$ < 2 Hz, =*C*Ph). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 33.15 ($^{1}J_{SeP}$ = 714.2 Hz).

4.1.3. Bis[2-(4-tert-butylphenyl)ethyl](2-phenylvinyl)phosphine selenide (**6c**)

Waxy product, yield 80%, *Z*:E = 75:25. Anal. Calc. for $C_{32}H_{41}PSe$: C, 71.76; H, 7.72; P, 5.78; Se, 14.74. Found: C, 72.02; H, 7.99; P, 5.89; Se, 14.48%. IR (film, ν, cm^{-1}): 1655 (C=C), 476 (P=Se). NMR for ***Z*-isomer**: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.29 (s, 18H, Me), 2.37 (m, 4H, CH_2P), 2.85 (m, 4H, $CH_2C_6H_4$), 6.01 (dd, $^{2}J_{HP}$ = 17.9 Hz, $^{3}J_{HH}$ = 13.4 Hz, 1H, =CHP), 6.91 (m, H_o, 4H, C_6H_4), 7.25-7.46 (m, 7H, H_m, H_p, PhC=, H_m, C_6H_4), 7.28 (dd, $^{3}J_{HP}$ = 41.2 Hz, $^{3}J_{HH}$ = 13.4 Hz, 1H, =CHPh), 7.89 (m, H_o, 2H, PhC=). ^{13}C NMR (100.69 MHz, $CDCl_3$): δ 28.86 (d, $^{2}J_{CP}$ = 3.2 Hz, $CH_2C_6H_4$), 31.25 (Me), 33.90 (d, $^{1}J_{CP}$ = 43.9 Hz, CH_2P), 34.23 (CMe_3), 121.33 (d, $^{1}J_{CP}$ = 63.1 Hz, =CP), 125.3 (C_m, C_6H_4), 128.08 (C_o, C_6H_4), 128.69 (C_m, PhC=), 129.50 (C_p, PhC=), 129.58 (C_o, PhC=), 135.71 (d, $^{3}J_{CP}$ = 6.4 Hz, C_i, PhC=), 137.03 (d, $^{3}J_{CP}$ = 14.8 Hz, C_i, C_6H_4), 145.15 (d, $^{2}J_{CP}$ = 3.6 Hz, =*C*Ph), 149.15 (C_p, C_6H_4). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 20.75. ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ -248.3 ($^{1}J_{SeP}$ = 688.4 Hz). NMR for ***E*-isomer**: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.29 (s, 18H, Me), 2.38 (m, 4H, CH_2P), 2.87 (m, 4H, $CH_2C_6H_4$), 6.35 (dd, $^{2}J_{HP}$ = 21.8 Hz, $^{3}J_{HH}$ = 16.4 Hz, 1H, =CHP), 6.91 (m, H_o, 4H, C_6H_4), 7.25–7.46 (m, 9H, H_m, C_6H_4, PhC=, H_o, H_m, H_p, PhC=), 7.60 (dd, $^{3}J_{HP}$ = 23.2 Hz, $^{3}J_{HH}$ = 16.4 Hz, 1H, =CHPh). ^{13}C NMR (100.69 MHz, $CDCl_3$): δ 28.55 (d, $^{2}J_{CP}$ = 2.0 Hz, $CH_2C_6H_4$), 31.25 (Me), 34.10 (d, $^{1}J_{CP}$ = 46.7 Hz, CH_2P), 34.23 (CMe_3), 117.01 (d, $^{1}J_{CP}$ = 67.5 Hz, =CP), 125.3 (C_m, C_6H_4), 128.30 (C_o, C_6H_4), 128.69 (C_o, PhC=), 128.90 (C_m, PhC=), 130.10 (C_p, PhC=), 134.75 (d, $^{3}J_{CP}$ = 18.8 Hz, C_i, PhC=), 137.26 (d, $^{3}J_{CP}$ = 14.0 Hz, C_i, C_6H_4), 149.11 (C_p, C_6H_4), 150.25 (d, $^{2}J_{CP}$ = 6.0 Hz, =*C*Ph). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 33.50. ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ -420.1 ($^{1}J_{SeP}$ = 712.0 Hz).

4.1.4. Bis[2-(2-pyridyl)ethyl](Z-2-phenylvinyl)phosphine selenide (**6d**)

Waxy product, yield 60%, *Z*:E = 95:5. Anal. Calc. for $C_{22}H_{23}N_2PSe$: C, 62.12; H, 5.45; N, 6.59; P, 7.28; Se, 18.56. Found: C, 62.39; H, 5.72; P, 7.01; Se, 18.28%. IR (film, ν, cm^{-1}): 1591 (C=C), 468 (P=Se). NMR for ***Z*-isomer**: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.46 (m, 4H, CH_2P), 3.02 (m, 4H, CH_2Py), 6.03 (dd, $^{2}J_{PH}$ = 18.6 Hz, $^{3}J_{HH}$ 13.7 Hz, 1H, =CHP), 6.97 (m, 2H, H_3, Py), 7.08 (m, 2H, H_5, Py), 7.25 (dd, $^{3}J_{HP}$ = 41.3 Hz, $^{3}J_{HH}$ = 13.7 Hz, 1H, =CHPh), 7.32 (m, 1H, H_p, PhC=), 7.38 (m, 2H, H_m, PhC=), 7.53 (m, 2H, H_4, Py), 7.83 (m, 2H, H_o, PhC=), 8.45 (m, 2H, H_6, Py). ^{13}C NMR (100.69 MHz, $CDCl_3$): δ 30.57 (d, $^{1}J_{CP}$ = 45.2 Hz, CH_2P), 31.56 (CH_2Py), 121.40 (d, $^{1}J_{CP}$ = 60.0 Hz, =CP), 121.60 (C_5, Py), 122.83

(C_3, Py), 128.40 (C_m, PhC=), 129.50 (C_p, PhC=), 129.69 (C_o, PhC=), 135.82 (d, $^3J_{CP}$ = 6.1 Hz, C_i, PhC=), 136.40 (C_4, Py), 145.40 (d, $^2J_{CP}$ = 2.5 Hz, =*C*Ph), 149.20 (C_6, Py), 159.70 (C_2, Py). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 22.3. ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ −252.2 ($^1J_{SeP}$ = 692.9 Hz).

4.2. Synthesis and characteristics of alkenylphosphine selenides **6a, c, e–f** under UV-initiation: typical procedure (Table 2)

A solution of phosphine selenide **1–3** and acetylene **5, 7, 8** (their molar ratio was 1:1) in dioxane was placed in a quartz ampoule under an argon atmosphere and irradiated (200-W Hg arc lamp) for the time indicated in Table 2. The solvent was then removed under vacuum, the residue was purified as described above.

4.2.1. [2-(2-Naphthyl)vinyl](diphenyl)phosphine selenide (**6e**)

Waxy product, yield 53%, *Z*:E = 60:40. Anal. Calc. for $C_{24}H_{19}PSe$: C, 69.07; H, 4.59; P, 7.42; Se, 18.92. Found: C, 68.79; H, 4.82; P, 7.14; Se, 18.64%. IR (film, ν, cm^{-1}): 1650 (C=C), 477 (P=Se). NMR for ***Z*-isomer**: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 6.50 (dd, $^2J_{HP}$ = 18.1 Hz, $^3J_{HH}$ = 13.5 Hz, 1H, =CHP), 7.50 (dd, $^3J_{HP}$ = 43.1 Hz, $^3J_{HH}$ = 13.5 Hz, 1H, =CHNaphthyl), 7.18–7.52, 7.78–8.10 (m, 17H, Ph, Naphthyl). ^{13}C NMR (100.69 MHz, $CDCl_3$): δ 122.60 (d, $^1J_{CP}$ = 73.9 Hz, =CP), 126.36-133.12 (Ph, Naphthyl), 145.81 (d, $^2J_{CP}$ = 2.0 Hz, =*C*Naphthyl). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 20.33. ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ −261.2 ($^1J_{SeP}$ = 717.1 Hz). NMR for ***E*-isomer**: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.02 (dd, $^2J_{HP}$ = 19.8 Hz, $^3J_{HH}$ = 16.6 Hz, 1H, =CHP), 7.67 (dd, $^3J_{HP}$ = 22.8 Hz, $^3J_{HH}$ = 16.6 Hz, 1H, =CHNaphthyl), 7.18–7.52, 7.78–8.10 (m, 17H, Ph, Naphthyl). ^{13}C NMR (100.69 MHz, $CDCl_3$): δ 118.90 (d, $^1J_{CP}$ = 77.9 Hz, =CP), 126.36–133.12 (Ph, Naphthyl), 148.99 (d, $^2J_{CP}$ = 7.2 Hz, =*C*Naphthyl). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 29.18. ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ −310.3 ($^1J_{SeP}$ = 727.0 Hz).

4.2.2. [2-(2-Naphthyl)vinyl][bis(2-phenylethyl)]phosphine selenide (**6f**)

Waxy product, yield 74%, *Z*:E = 50:50. Anal. Calc. for $C_{28}H_{27}PSe$: C, 71.03; H, 5.75; P, 6.54; Se, 16.68. Found: C, 70.79; H, 5.98; P, 6.30; Se, 16.97%. IR (film, ν, cm^{-1}): 1658 (C=C), 477 (P=Se). NMR for ***Z*-isomer**: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.25 (m, 4H, CH_2P), 2.76 (m, 4H, CH_2Ph), 6.03 (dd, $^2J_{HP}$ = 18.1 Hz, $^3J_{HH}$ = 13.5 Hz, 1H, =CHP), 6.83 (m, 4H, Ho, PhCH_2), 7.42 (dd, $^3J_{HP}$ = 41.1 Hz, $^3J_{HH}$ = 13.5 Hz, 1H, =CHNaphthyl), 7.07–7.91 (m, 12H, Ph, Naphthyl), 8.49 (s, 1H, H_1, Naphthyl). ^{13}C NMR (100.69 MHz, $CDCl_3$): δ 29.57 (d, $^2J_{CP}$ = 3.0 Hz, CH_2Ph), 33.28 (d, $^1J_{CP}$ = 44.7 Hz, CH_2P), 121.49 (d, $^1J_{CP}$ = 63.8 Hz, =CP), 126.03-129.63 (Ph, Naphthyl), 133.18 (d, $^3J_{CP}$ = 6.6 Hz, C_2, Naphthyl), 140.21 (d, $^3J_{CP}$ = 15.4 Hz, C_i, Ph), 145.56 (d, =*C*Naphthyl, $^2J_{CP}$ = 3.0 Hz, =*C*Naphthyl). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 20.91 ($^1J_{SeP}$ = 688.4 Hz). NMR for ***E*-isomer**: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.40 (m, 4H, CH_2P), 2.99 (m, 4H, CH_2Ph), 6.38 (dd, $^2J_{HP}$ = 21.7 Hz, $^3J_{HH}$ = 16.6 Hz, 1H, =CHP), 7.74 (dd, $^3J_{HP}$ = 23.3 Hz, $^3J_{HH}$ = 16.6 Hz, 1H, =CHPh), 7.07–7.91 (m, 17H, Ph, Naphthyl). ^{13}C NMR (100.69 MHz, $CDCl_3$): δ 29.26 (d, $^2J_{CP}$ < 2 Hz, CH_2Ph), 34.39 (d, $^1J_{CP}$ = 47.0 Hz, CH_2P), 116.80 (d, $^1J_{CP}$ = 68.2 Hz, =CP), 123.88 (C_1, Naphthyl), 126.03-129.63 (Ph, Naphthyl), 132.20 (d, $^3J_{CP}$ = 19.1 Hz, C_2, Naphthyl), 140.54 (d, $^3J_{CP}$ = 15.4 Hz, C_i, Ph), 150.98 (d, $^2J_{CP}$ = 6.6 Hz, =*C*Naphthyl). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 33.42 ($^1J_{SeP}$ = 713.1 Hz).

4.2.3. [2-(2-Furyl)vinyl][bis(2-phenylethyl)]phosphine selenide (**6g**)

Waxy product, yield 60%, *Z*:E = 35:65. Anal. Calc. for $C_{22}H_{23}OPSe$: C, 63.93; H, 5.61; P, 7.49; Se, 19.10. Found: C, 63.65; H, 5.89; P, 7.68; Se, 19.38%. IR (film, ν, cm^{-1}): 1663 (C=C), 470 (P=Se). NMR for ***Z*-isomer**: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.27 (m, 4H, CH_2P), 3.31 (m, 4H, CH_2Ph), 5.79 (dd, $^2J_{HP}$ = 14.0 Hz, $^3J_{HH}$ = 14.2 Hz, 1H, =CHP), 6.50 (dd, $^3J_{3-4}$ = 3.4 Hz, $^3J_{4-5}$ = 1.7 Hz, 1H, H_4, furyl), 6.77 (dd, $^3J_{HP}$ = 39.4 Hz, $^3J_{HH}$ = 14.2 Hz, 1H, =CH-furyl), 6.84 (dd, $^3J_{3-4}$ = 3.4 Hz, $^4J_{3-5}$ = 1.0 Hz, 1H, H_3, furyl), 7.07–7.27 (m, 10H, Ph), 7.51 (dd, $^3J_{4-5}$ = 1.7 Hz, $^4J_{3-5}$ = 1.0 Hz, 1H, H_5, furyl). ^{13}C NMR (100.69 MHz, $CDCl_3$): δ 29.49 (CH_2Ph), 34.13 (d, $^1J_{CP}$ = 45.6 Hz, CH_2P), 112.59 (C_4, furyl), 117.01 (C_3, furyl), 117.60 (d, $^1J_{CP}$ = 62.3 Hz, =CP), 126.58 (C_p, Ph), 128.33 (C_m, Ph), 128.64 (C_o, Ph), 130.09 (d, $^2J_{CP}$ = 7.6 Hz, =*C*-furyl), 140.74 (d, $^3J_{CP}$ = 15.3 Hz, C_i, Ph), 144.63 (C_5, furyl), 150.18 (d, $^3J_{CP}$ = 8.4 Hz, C_2, furyl). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 24.70 ($^1J_{SeP}$ = 690.1 Hz). NMR for ***E*-isomer**: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.30 (m, 4H, CH_2P), 2.91 (m, 4H, CH_2Ph), 6.23 (dd, $^2J_{HP}$ = 21.8 Hz, $^3J_{HH}$ = 16.4 Hz, 1H, =CHP), 6.43 (dd, $^3J_{3-4}$ = 3.2 Hz, $^3J_{4-5}$ = 1.7 Hz, 1H, H_4, furyl), 6.54 (dd, $^3J_{3-4}$ = 3.2 Hz, $^4J_{3-5}$ = 1.0 Hz, 1H, H_3, furyl), 7.07–7.27 (m, 10H, Ph), 7.41 (dd, $^3J_{HP}$ = 22.7 Hz, $^3J_{HH}$ = 16.4 Hz, 1H, =CH—furyl), 7.42 (dd, $^3J_{4-5}$ = 1.7 Hz, $^4J_{3-5}$ = 1.0 Hz, 1H, H_5, furyl). ^{13}C NMR (100.69 MHz, $CDCl_3$): δ 29.14 (CH_2Ph), 34.34 (d, $^1J_{CP}$ = 48.0 Hz, CH_2P), 112.17 (C_4, furyl), 113.79 (d, $^1J_{CP}$ = 69.5 Hz, =CP), 113.96 (C_3, furyl), 126.36 (C_p, Ph), 128.24 (C_m, Ph), 128.56 (C_o, Ph), 137.70 (d, $^2J_{CP}$ = 7.6 Hz, =*C*—furyl), 140.47 (d, $^3J_{CP}$ = 15.7 Hz, C_i, Ph), 144.26 (C_5, furyl), 151.22 (d, $^3J_{CP}$ = 22.0 Hz, C_2, furyl). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 33.72 ($^1J_{SeP}$ = 714.2 Hz).

4.3. Synthesis and characteristics of (2-phenylvinyl)[bis(2-phenylethyl)]phosphine (**9**)

To a solution of phosphine selenide **6b** (317 mg, 0.75 mmol) in 7.5 ml of toluene metal sodium (86 mg, 3.74 mmol) was added. The reaction mixture was refluxed under an argon atmosphere for 0.5 h, then cooled and filtered. After removal of toluene under vacuum phosphine **9** (250 mg, 97%) was prepared as a waxy product, *Z*:*E* = 80:20. Anal. Calc. for $C_{24}H_{25}P$: C, 83.69; H, 7.32; P, 8.99. Found: C, 83.40; H, 7.07; P, 8.69%. NMR for ***Z*-isomer**: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.82 (m, 4H, CH_2P), 2.71 (m, 4H, CH_2Ph), 6.03 (dd, $^2J_{HP}$ = 3.1 Hz, $^3J_{HH}$ = 12.8 Hz, 1H, =CHP), 7.08–7.60 (m, 16H, =CHPh, Ph). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ −41.48. NMR for ***E*-isomer**: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.84 (m, 4H, CH_2P), 2.72 (m, 4H, CH_2Ph), 6.53 (dd, $^3J_{HP}$ = 3.1 Hz, $^3J_{HH}$ = 17.2 Hz, 1H, =CHP), 6.98 (dd, $^3J_{HP}$ = 13.3 Hz, $^3J_{HH}$ = 17.2 Hz, 1H, =CHPh), 7.08–7.60 (m, 15H, Ph). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ -26.40. MS (EI), *m/z*: 344 (M^+), 343, 315, 239, 237, 212, 149, 136, 133, 115, 105, 91, 77, 65, 51.

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