A Facile Atom-Economic Synthesis of Imidazoles with Chalcogenophosphoryl Substituents via Free-Radical Addition of Secondary Phosphine Chalcogenides to 1-Vinylimidazoles

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Abstract: Secondary phosphine sulfides and selenides react with 1-vinylimidazoles under radical initiation conditions to give the corresponding anti-Markovnikov adducts in up to 98% yields.

Key words: 1-vinylimidazoles, phosphine sulfides, phosphine selenides, radical addition

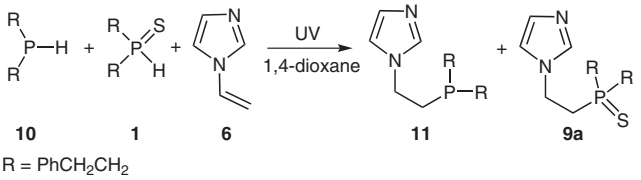
The imidazole ring is found frequently in natural products and biologically active compounds[1] such as biotin, histamine, the essential amino acid histidine, and the pilocarpine alkaloids. Imidazole-tailored ionic liquids[1f,2] and organic catalysts[3] are other applications of imidazole derivatives. Significant interest has focused on the synthesis of functionalized imidazoles containing organophosphorus substituents that are used as polydentate ligands for the design of effective metal–complex catalysts.[4] Recently, we reported the synthesis of 1-substituted imidazoles possessing phosphinyl moieties via radical addition of secondary phosphines to 1-vinylimidazoles.[5]

Herein, we report a strategy for the simple and atom-economic synthesis of novel families of functionalized imidazoles. To achieve this goal we have examined, for the first time, the reaction of 1-vinylimidazoles with secondary phosphine chalcogenides. These substrates were prepared from red phosphorus, styrenes and elemental chalcogens.[6]

Our experiments revealed that secondary phosphine sulfides **1** and **2** and phosphine selenides **3**–**5** reacted readily with 1-vinylimidazole (**6**), 2-methyl-1-vinylimidazole (**7**) and 1-vinylbenzimidazole (**8**) under UV irradiation, or in the presence of 2,2′-azobis(isobutyronitrile) (AIBN) at 65–70 °C to form regioselectively the corresponding anti-Markovnikov adducts **9a**–**k** in high yields (Table 1).

It is pertinent to mention that secondary phosphine oxides do not react with vinylimidazoles **6**–**8** under the above conditions.[5] This fact correlates well with the low reactivity of secondary phosphine oxides in the presence of radical initiators[7] due to the high P–H bond dissociation energy in the phosphoryl moiety.[8]

Analysis of the results obtained (Table 1), as well as published data,[5] showed that the reactivities of secondary phosphine sulfides and phosphine selenides were higher than those of the corresponding phosphines. Hence, the reactions with phosphine chalcogenides **1**–**5** (Table 1) were complete within 1.5–4 hours; in contrast, the corresponding secondary phosphines required reaction times of 2–7 hours.[5] To evaluate the comparative reactivity of these PH-adducts with vinylimidazoles under radical addition conditions, we studied the competitive reaction of bis(2-phenylethyl)phosphine (**10**) and bis(2-phenylethyl)phosphine sulfide (**1**) with 1-vinylimidazole (**6**). Thus, a solution of compounds **1**, **6** and **10** (molar ratio = 1:1:1) in 1,4-dioxane was subjected to UV irradiation in a quartz tube under an argon atmosphere. The relative rates of conversion of PH-adducts **1** and **10**, and formation of the corresponding imidazolylphosphine **11** and imidazolylphosphine sulfide **9a** (Scheme 1) were monitored by ^{31}P NMR spectroscopy.



Scheme 1 Competitive reaction of secondary phosphine **10** and phosphine sulfide **1** with 1-vinylimidazole (**6**)

The data obtained proved that phosphine sulfide **1** was more active in the reaction with 1-vinylimidazole (**6**) than bis(2-phenylethyl)phosphine (**10**). In the first 30 minutes of the reaction the concentration of the formed tertiary phosphine sulfide **9a** was almost 1.80 times higher than that of tertiary phosphine **11**. After 60 minutes, this ratio increased to 2.10, and after 90 minutes to 2.75; the concentration of the initial phosphine sulfide **1** being diminished faster than that of secondary phosphine **10**. The higher reactivity of secondary phosphine sulfides and selenides compared to secondary phosphines in free-radical additions to the electron-rich double bond of vinyl ethers, under radical initiation, has been reported previously.[9]

To summarize, the reported free-radical addition of secondary phosphine sulfides and phosphine selenides to 1-vinylimidazoles represents a simple and atom-economic synthesis of a novel family of functionalized imidazoles possessing chalcogenophosphoryl moieties. These com-

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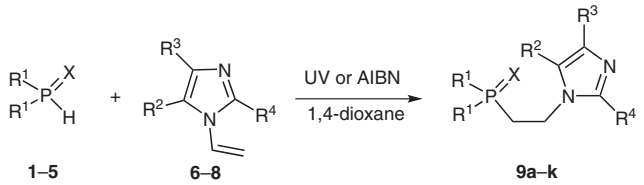
pounds are promising candidates for drug design and as polydentate ligands for the preparation of effective metal–complex catalysts. The reaction developed may be considered as a basic contribution to both imidazole and organophosphorus chemistry.

Table 1 Addition of Secondary Phosphine Chalcogenides **1–5** to Imidazoles **6–8**[a]



1–5 **6–8** **9a–k**

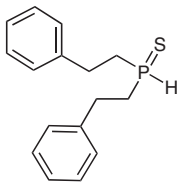
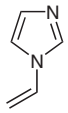
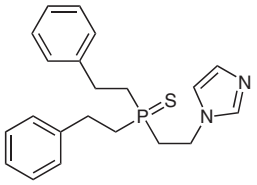
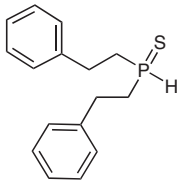
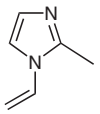
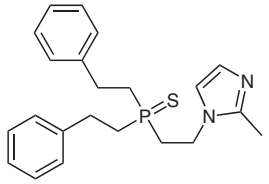
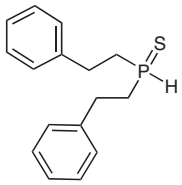
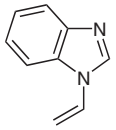
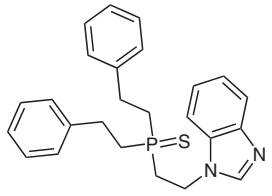
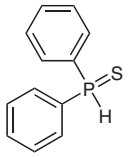
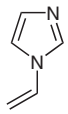
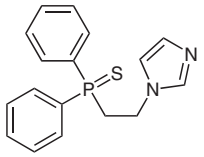
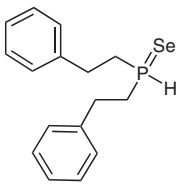
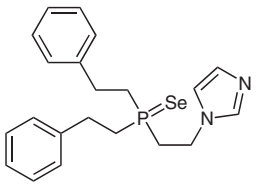
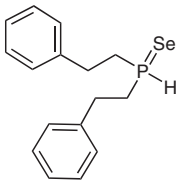
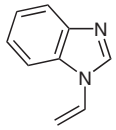
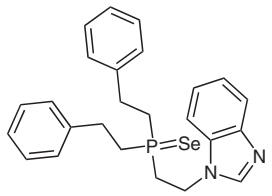
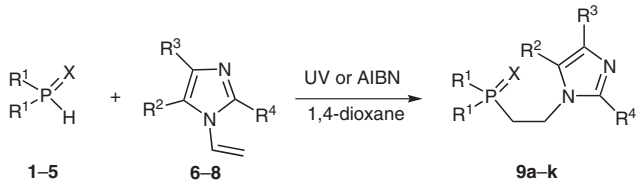
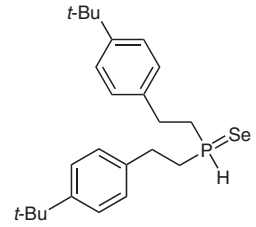
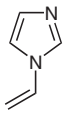
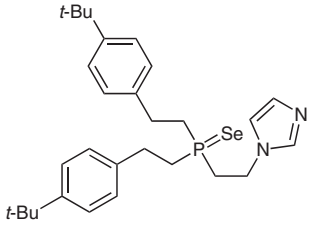
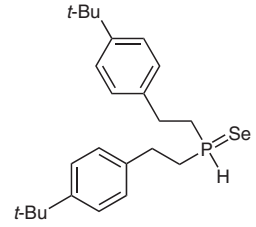
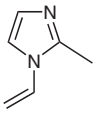
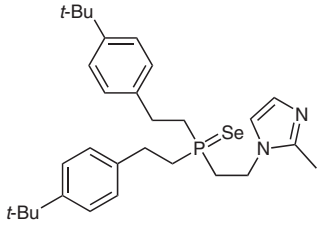
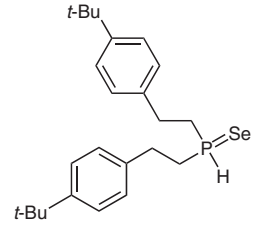
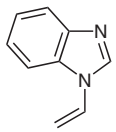
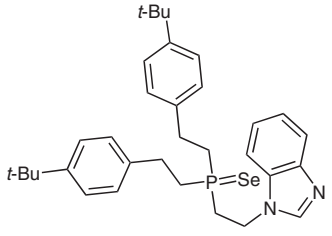
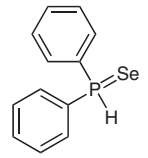
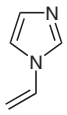
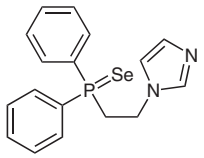
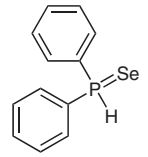
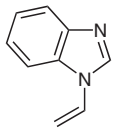
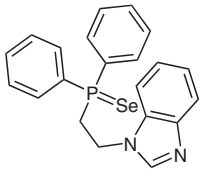
Entry	PH-adduct	Imidazole	Product	Conditions	Yield (%)[b]
1	 **1**	 **6**	 **9a**	UV, 2 h AIBN, 4 h	98 93
2	 **1**	 **7**	 **9b**	UV, 2 h	96
3	 **1**	 **8**	 **9c**	UV, 2 h	91
4	 **2**	 **6**	 **9d**	UV, 1.5 h	94
5	 **3**	 **6**	 **9e**	UV, 1.5 h AIBN, 3 h	98 80
6	 **3**	 **7**	 **9f**	UV, 2 h	95

Table 1 Addition of Secondary Phosphine Chalcogenides **1–5** to Imidazoles **6–8**[a] (continued)



1–5 **6–8** **9a–k**

Entry	PH-adduct	Imidazole	Product	Conditions	Yield (%)[b]
7	 **4**	 **6**	 **9g**	UV, 2 h	96
8	 **4**	 **7**	 **9h**	UV, 1.5 h	98
9	 **4**	 **8**	 **9i**	UV, 3 h	95
10	 **5**	 **6**	 **9j**	UV, 1.5 h	95
11	 **5**	 **8**	 **9k**	UV, 2 h	90

[a] The ratio of PH-adduct–imidazole was 1:1. All experiments were carried out under an Ar atmosphere.
[b] Yield of isolated product.

All reactions were carried out under an Ar atmosphere. 1,4-Dioxane was distilled and dried according to a standard procedure. Diphenylphosphine and 1-vinylimidazole (**6**) were obtained from Aldrich Chemical Co. Diphenylphosphine chalcogenides **2** and **5** were prepared by oxidation of diphenylphosphine with elemental S or Se powder in EtOH. 1-Vinylimidazole (**6**) was distilled under reduced pressure prior to use. 2-Methyl-1-vinylimidazole (**7**) and 1-vinylbenzylimidazole (**8**) were synthesized using literature methods.[10] AIBN was recrystallized from EtOH prior to use. UV irradiation experiments were carried out using a 200 W mercury arc lamp. Melting points were recorded on a Stuart melting point apparatus and are uncorrected. IR spectra were obtained using Bruker Vertex 70 instrumentation. ^{1}H, ^{13}C, ^{31}P and ^{77}Se NMR spectra were recorded at 400.13, 100.62, 161.98 and 76.31 MHz, respectively, as $CDCl_3$ solutions, on a Bruker DPX-400 spectrometer. Chemical shifts are reported in δ (ppm) relative to the residual non-deuterated ($CHCl_3$)

solvent signal (^{1}H, ^{13}C) as the internal standard, or H_3PO_4 (^{31}P) and Me_2Se (^{77}Se) as external standards. Elemental analyses were obtained using a ThermoFinnigan CHN Flash EA1112 analyzer.

Tertiary Phosphine Sulfides 9a–d and Phosphine Selenides 9e–k; General Procedure

A soln of phosphine chalcogenide **1**–**5** (1.0 mmol) and imidazole **6**–**8** (1.0 mmol) in 1,4-dioxane (0.5 mL) was irradiated (200 W Hg arc lamp) in a quartz ampoule (method A), or heated at 65–70 °C in the presence of AIBN (1% wt of the total mass of reactants) in a sealed ampoule (method B) (reaction times are given in Table 1). The reaction progress was monitored using ^{31}P NMR spectroscopy; the disappearance of the signal due to the starting phosphine chalcogenides (20–24 ppm for sulfides **1**–**2** and 2–8 ppm for selenides **3**–**5**), and the appearance of a new resonance at 46–48 ppm and 30–36 ppm for the tertiary phosphine sulfides **9a**–**d** and phosphine selenides **9e**–**k**, being indicative of completion. The mixture was dissolved in Et_2O (3 mL), filtered through a layer of Al_2O_3 (activity level II, 0.5 cm), and the filter-bed washed with a mixture of hexane–Et_2O (3 mL, 1:1). The solvents were removed by distillation under reduced pressure to give phosphine chalcogenides **9a**–**k**.

[2-(1*H*-Imidazol-1-yl)ethyl]diphenethylphosphine Sulfide (9a)

Light-yellow oil; yield (method A): 361 mg (98%); yield (method B): 343 mg (93%).

IR (film): 3086, 3062, 2933, 1603, 1497, 1454, 1403, 1359, 1288, 1230, 1181, 1108, 1078, 1030, 965, 947, 907, 818, 753, 699, 663, 622, 597, 551, 497 cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.91–2.17 (m, 6 H, CH_2P), 2.83–2.88 (m, 4 H, CH_2Ph), 4.23–4.30 (m, 2 H, CH_2N), 6.89 and 7.03 (s, 2 H, H-4,5, imidazole), 7.13–7.27 (m, 10 H, Ph), 7.60 (s, 1H, H-2, imidazole).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 28.45 (CH_2Ph), 31.98 (d, $^1J_{P–C}$ = 47.8 Hz, P*C*H_2CH$_2$N), 33.30 (d, $^1J_{P–C}$ = 49.3 Hz, CH_2P), 41.10 (CH_2N), 118.82 (C-4, imidazole), 126.77 (*p*-C, Ph), 128.24 (*o*-C, Ph), 128.77 (*m*-C, Ph), 129.27 (C-5, imidazole), 137.08 (C-2, imidazole), 139.97 (d, $^3J_{P–C}$ = 12.7 Hz, *i*-C, Ph).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 46.21.

Anal. Calcd for $C_{21}H_{25}N_2PS$: C, 68.45; H, 6.84; N, 7.60; P, 8.41; S, 8.70. Found: C, 68.40; H, 6.89; N, 7.45; P, 8.13; S, 8.32.

[2-(2-Methyl-1*H*-imidazol-1-yl)ethyl]diphenethylphosphine Sulfide (9b)

Colorless crystalline solid; yield (method A): 367 mg (96%); mp 128–130 °C (hexane).

IR (KBr): 3064, 3026, 2997, 2931, 2868, 1602, 1523, 1497, 1453, 1424, 1357, 1286, 1271, 1230, 1142, 1110, 1072, 1020, 967, 944, 915, 803, 775, 729, 699, 676, 603, 552, 496 cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.01–2.10 (m, 6 H, PCH_2), 2.40 (s, 3 H, Me), 2.87–2.89 (m, 4 H, CH_2Ph), 4.16–4.23 (m, 2 H, CH_2N), 6.81 and 6.89 (s, 2 H, H-4,5, imidazole), 7.14–7.23 (m, 10 H, Ph).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 12.84 (Me), 28.31 (CH_2Ph), 31.35 (d, $^1J_{P–C}$ = 47.8 Hz, P*C*H_2CH$_2$N), 33.10 (d, $^1J_{P–C}$ = 48.2 Hz, CH_2P), 39.85 (CH_2N), 118.96 (C-4, imidazole), 126.57 (*p*-C, Ph), 128.0 (*o*-C, Ph), 128.45 (C-5, imidazole), 128.60 (*m*-C, Ph), 139.76 (d, $^3J_{P–C}$ = 13.6 Hz, *i*-C, Ph), 144.06 (C-2, imidazole).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 46.10.

Anal. Calcd for $C_{22}H_{27}N_2PS$: C, 69.08; H, 7.11; N, 7.32; P, 8.10; S, 8.38. Found: C, 69.04; H, 7.09; N, 7.45; P, 8.30; S, 8.35.

[2-(1*H*-Benzo[*d*]imidazol-1-yl)ethyl]diphenethylphosphine Sulfide (9c)

Colorless crystalline solid; yield (method A): 381 mg (91%); mp 50–51 °C (hexane).

IR (KBr): 3085, 3062, 3005, 2931, 2859, 1614, 1496, 1454, 1403, 1366, 1332, 1284, 1242, 1217, 1161, 1009, 946, 872, 864, 750, 699, 666, 612, 551, 496, 427 cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.97–2.03 (m, 4 H, PCH_2), 2.23–2.28 (m, 2 H, PCH_2CH$_2$N), 2.75–2.84 (m, 4 H, CH_2Ph), 4.51–4.59 (m, 2 H, CH_2N), 7.03 and 7.05 (m, 2 H, H-5,6, imidazole), 7.14–7.32 (m, 10 H, Ph), 7.43, 7.79 and 8.09 (m, 3 H, H-4,7,2, imidazole).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 28.59 (CH_2Ph), 30.01 (d, $^1J_{P–C}$ = 49.6 Hz, P*C*H_2CH$_2$N), 33.62 (d, $^1J_{P–C}$ = 52.4 Hz, CH_2P), 39.38 (CH_2N), 109.75 (C-7, imidazole), 120.54, 122.89 and 123.62 (C-4, 6, 5, imidazole), 126.80 (*p*-C, Ph), 128.31 (*o*-C, Ph), 128.83 (*m*-C, Ph), 133.05 (C-8, imidazole), 140.02 (d, $^3J_{P–C}$ = 12.0 Hz, *i*-C, Ph), 143.25 and 143.36 (C-2,9, imidazole).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 47.57.

Anal. Calcd for $C_{25}H_{27}N_2PS$: C, 71.74; H, 6.50; N, 6.69; P, 7.40; S, 7.66. Found: C, 71.69; H, 6.49; N, 6.65; P, 7.36; S 7.54.

[2-(1*H*-Imidazol-1-yl)ethyl]diphenylphosphine Sulfide (9d)

Light-yellow oil; yield (method A): 294 mg (94%).

IR (film): 3139, 3054, 2923, 2852, 1672, 1586, 1509, 1481, 1437, 1400, 1181, 1105, 1035, 1021, 997, 845, 747, 709, 694, 628, 611, 560, 509, 492 cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.88–2.95 (m, 2 H, CH_2P), 4.36–4.42 (m, 2 H, CH_2N), 6.84 and 6.87 (s, 2 H, H-4,5, imidazole), 7.42–7.78 and 7.75–7.80 (m, 10 H, Ph), 7.87 (s, 1 H, H-2, imidazole).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 33.79 (d, $^1J_{P–C}$ = 53.8 Hz, CH_2P), 42.49 (CH_2N), 120.00 (C-4, imidazole), 128.77 (d,$^2J_{P–C}$ = 12.5 Hz, *o*-C, Ph), 130.00 (C-5, imidazole), 130.80 (d,$^3J_{P–C}$ = 11.3 Hz, *m*-C, Ph), 131.13 (d, $^1J_{P–C}$ = 87.4 Hz, *i*-C, Ph), 131.94 (*p*-C, Ph), 136.81 (C-2, imidazole).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 39.17.

Anal. Calcd for $C_{17}H_{17}N_2PS$: C, 65.37; H, 5.49; N, 8.97; P, 9.92; S, 10.27. Found: C, 65.31; H, 5.48; N, 8.90; P, 9.90; S, 10.20.

[2-(1*H*-Imidazol-1-yl)ethyl]diphenethylphosphine Selenide (9e)

Light-yellow oil; yield (method A): 407 mg (98%); yield (method B): 332 mg (80%).

IR (film): 3107, 3062, 3003, 2932, 1602, 1497, 1454, 1402, 1359, 1323, 1230, 1150, 1108, 1077, 1030, 965, 907, 818, 753, 699, 662, 621, 573, 495, 470, 454 cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.02–2.23 (m, 6 H, CH_2P), 2.82–2.91 (m, 4 H, CH_2Ph), 4.27–4.31 (m, 2 H, CH_2N), 6.90 and 7.03 (s, 2 H, H-4,5, imidazole), 7.14–7.30 (m, 10 H, Ph), 7.56 (s, 1 H, H-2, imidazole).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 29.22 (CH_2Ph), 31.30 (d, $^1J_{P–C}$ = 40.5 Hz, P*C*H_2CH$_2$N), 32.85 (d, $^1J_{P–C}$ = 41.7 Hz, CH_2P), 41.98 (CH_2N), 118.75 (C-4, imidazole), 126.77 (*p*-C, Ph), 128.23 (*o*-C, Ph), 128.78 (*m*-C, Ph), 129.64 (C-5, imidazole), 137.13 (C-2, imidazole), 139.69 (d, $^3J_{P–C}$ = 13.1 Hz, *i*-C, Ph).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 35.28 (s + d satellites, $^1J_{P–Se}$ = 710 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –392.10 (d, $^1J_{P–Se}$ = 710 Hz).

Anal. Calcd for $C_{21}H_{25}N_2PSe$: C, 60.72; H, 6.07; N, 6.74; P, 7.46; Se, 19.01. Found: C, 60.60; H, 6.09; N, 6.45; P, 7.30; Se, 18.92.

[2-(1*H*-Benzo[*d*]imidazol-1-yl)ethyl]diphenethylphosphine Selenide (9f)
Colorless crystalline solid; yield (method A): 442 mg (95%); mp 105–106 °C (hexane).

IR (KBr): 3084, 3057, 2919, 2862, 1601, 1496, 1453, 1444, 1383, 1362, 1331, 1282, 1251, 1220, 1197, 1162, 1010, 956, 866, 842, 770, 761, 741, 699, 653, 626, 570, 452 cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 2.04–2.10 (m, 4 H, PCH_2), 2.27–2.34 (m, 2 H, PCH_2CH_2N), 2.72–2.82 (m, 4 H, CH_2Ph), 4.49–4.56 (m, 2 H, CH_2N), 7.00 and 7.02 (s, 2 H, H-5,6, imidazole), 7.16–7.27 (m, 10 H, Ph), 7.40, 7.77 and 8.00 (m, 3 H, H-4,7,2, imidazole).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 29.14 (d, $^1J_{P-C}$ = 40.7 Hz, PCH_2CH_2N), 29.16 (CH_2Ph), 33.87 (d, $^1J_{P-C}$ = 41.4 Hz, CH_2P), 40.09 (CH_2N), 109.49 (C-7, imidazole), 120.54, 122.55 and 123.29 (C-4, 6, 5, imidazole), 126.66 (*p*-C, Ph), 128.17 (*o*-C, Ph), 128.71 (*m*-C, Ph), 132.87 (C-8, imidazole), 139.55 (d, $^3J_{P-C}$ = 13.2 Hz, *i*-C, Ph), 143.05 and 143.62 (C-2, 9, imidazole).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 35.59 (s + d satellites, $^1J_{P-Se}$ = 715 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –388.10 (d, $^1J_{P-Se}$ = 715 Hz).

Anal. Calcd for $C_{25}H_{27}N_2PSe$: C, 64.51; H, 5.85; N, 6.02; P, 6.65; Se, 16.96. Found: C, 64.50; H, 5.82; N, 6.00; P, 6.63; Se, 16.92.

[2-(1*H*-Imidazol-1-yl)ethyl]bis[4-(*tert*-butyl)phenethyl]phosphine Selenide (9g)
Light-yellow oil; yield (method A): 506 mg (96%).

IR (film): 3095, 3055, 2963, 2867, 1709, 1509, 1463, 1444, 1404, 1394, 1364, 1269, 1219, 1140, 1108, 1079, 1019, 963, 817, 756, 663, 622, 564, 484 cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.26 (s, 18 H, Me), 2.07–2.25 (m, 6 H, CH_2P), 2.80–2.86 (m, 4 H, CH_2Ph), 4.25–4.32 (m, 2 H, CH_2N), 6.88 and 7.02 (s, 2 H, H-4,5, imidazole), 7.09 and 7.27 (m, 8 H, Ph), 7.57 (s, 1 H, H-2, imidazole).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 28.66 (CH_2Ph), 31.14 (d, $^1J_{P-C}$ = 40.0 Hz, PCH_2CH_2N), 31.24 (Me), 32.63 (d, $^1J_{P-C}$ = 40.7 Hz, CH_2P), 34.34 (*C*Me), 41.95 (CH_2N), 118.76 (C-4, imidazole), 125.61 (*o*-C, Ph), 127.87 (*m*-C, Ph), 129.42 (C-5, imidazole), 136.54 (d, $^3J_{P-C}$ = 15.9 Hz, *i*-C, Ph), 137.03 (C-2, imidazole), 149.61 (*p*-C, Ph).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 35.58 (s + d satellites, $^1J_{P-Se}$ = 708 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –392.1 (d, $^1J_{P-Se}$ = 708 Hz).

Anal. Calcd for $C_{29}H_{41}N_2PSe$: C, 66.02; H, 7.83; N, 5.31; P, 5.87; Se, 14.97. Found: C, 66.00; H, 7.80; N, 5.32; P, 5.56; Se 14.72.

Bis[4-(*tert*-butyl)phenethyl][2-(2-methyl-1*H*-imidazol-1-yl)ethyl]phosphine Selenide (9h)
Colorless crystalline solid; yield (method A): 531 mg (98%); mp 95–96 °C (hexane).

IR (KBr): 3092, 3054, 2963, 2904, 2865, 1577, 1501, 1454, 1426, 1363, 1269, 1214, 1145, 1108, 1073, 1021, 1000, 977, 871, 854, 840, 773, 734, 677, 571, 560, 523, 482, 462 cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.27 (s, 18 H, Me), 2.13–2.22 (m, 6 H, CH_2P), 2.41 (s, 3 H, Me), 2.81–2.88 (m, 4 H, CH_2Ar), 4.15–4.22 (m, 2 H, CH_2N), 6.79 and 6.89 (s, 2 H, H-4,5, imidazole), 7.08 and 7.30 (m, 8 H, Ph).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 13.06 (Me), 28.65 (CH_2Ph), 30.46 (d, $^1J_{P-C}$ = 42.5 Hz, PCH_2CH_2N), 31.19 (Me), 32.68 (d, $^1J_{P-C}$ = 44.5 Hz, CH_2P), 34.29 (*C*Me), 40.92 (CH_2N), 118.88 (C-4, imidazole), 125.53 (*o*-C, Ph), 127.27 (C-5, imidazole), 127.75 (*m*-C, Ph), 136.44 (d, $^3J_{P-C}$ = 13.6 Hz, *i*-C, Ph), 144.17 (C-2, imidazole), 149.70 (*p*-C, Ph).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 34.90 (s + d satellites, $^1J_{P-Se}$ = 705 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –388.9 (d, $^1J_{P-Se}$ = 706 Hz).

Anal. Calcd for $C_{30}H_{43}N_2PSe$: C, 66.53; H, 8.00; N, 5.17; P, 5.72; Se, 14.58. Found: C, 66.47; H, 8.04; N, 5.15; P, 5.43; Se, 14.50.

[2-(1*H*-Benzo[*d*]imidazol-1-yl)ethyl]bis[4-(*tert*-butyl)phenethyl]phosphine Selenide (9i)
Colorless crystalline solid; yield (method A): 549 mg (95%); mp 170–173 °C (hexane).

IR (KBr): 3093, 3054, 2962, 2865, 1615, 1493, 1461, 1363, 1283, 1268, 1247, 1199, 1163, 1142, 1108, 1009, 928, 865, 827, 811, 768, 745, 563, 430, 416 cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.25 (s, 18 H, Me), 2.04–2.12 (m, 4 H, CH_2P), 2.28–2.39 (m, 2 H, PCH_2CH_2N), 2.68–2.87 (m, 4 H, CH_2Ph), 4.51–4.61 (m, 2 H, CH_2N), 6.10–7.43 (m, 10 H, H-5,6, imidazole, Ph), 7.44, 7.80 and 7.96 (m, 3 H, H-4,7,2, imidazole).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 28.36 (CH_2Ph), 28.90 (d, $^1J_{P-C}$ = 41.9 Hz, PCH_2CH_2N), 30.90 (Me), 32.53 (d, $^1J_{P-C}$ = 41.9 Hz, CH_2P), 34.04 (*C*Me), 39.84 (CH_2N), 109.08, 120.38 and 122.20 (C-7, 6, 5, imidazole), 125.25 (*o*-C, Ph), 127.52 (*m*-C, Ph), 132.70 (C-8, imidazole), 136.11 (d, $^3J_{P-C}$ = 13.6 Hz, *i*-C, Ph), 142.62 and 143.58 (C-2, 9, imidazole), 149.35 (*p*-C, Ph).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 35.42 (s + d satellites, $^1J_{P-Se}$ = 709 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –391.8 (d, $^1J_{P-Se}$ = 709 Hz).

Anal. Calcd for $C_{33}H_{43}N_2PSe$: C, 68.62; H, 7.50; N, 4.85; P, 5.36; Se, 13.67. Found: C, 68.59; H, 7.49; N, 4.79; P, 5.31; Se, 13.58.

[2-(1*H*-Imidazol-1-yl)ethyl]diphenylphosphine Selenide (9j)
Light-yellow oil; yield (method A): 340 mg (95%).

IR (film): 3110, 3053, 2923, 2851, 1607, 1587, 1574, 1507, 1481, 1436, 1395, 1359, 1309, 1290, 1231, 1101, 1026, 997, 907, 845, 747, 692, 662, 623, 559, 541, 514, 495 cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 2.97–3.04 (m, 2 H, CH_2P), 4.35–4.41 (m, 2 H, CH_2N), 6.85 and 6.87 (s, 2 H, H-4,5, imidazole), 7.40–7.75 (m, 10 H, Ph), 7.94 (m, 1 H, H-2, imidazole).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 33.87 (d, $^1J_{P-C}$ = 47.5 Hz, CH_2P), 42.45 (CH_2N), 119.04 (C-4, imidazole), 128.90 (d, $^3J_{P-C}$ = 12.5 Hz, *o*-C, Ph), 130.27 (d, $^1J_{P-C}$ = 79.6 Hz, *i*-C, Ph), 130.54 (C-5, imidazole), 131.30 (d, $^2J_{P-C}$ = 10.7 Hz, *m*-C, Ph), 136.02 (d, $^4J_{P-C}$ = 2.1 Hz, *p*-C, Ph), 136.64 (C-2, imidazole).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 30.50 (s + d satellites, $^1J_{P-Se}$ = 735 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –357.1 (d, $^1J_{P-Se}$ = 735 Hz).

Anal. Calcd for $C_{17}H_{17}N_2PSe$: C, 56.83; H, 4.77; N, 7.80; P, 8.62; Se, 21.98. Found: C, 56.79; H, 4.72; N, 7.79; P, 8.59; Se, 21.93.

[2-(1*H*-Benzo[*d*]imidazol-1-yl)ethyl]diphenylphosphine Selenide (9k)
Light-yellow oil; yield (method A): 368 mg (90%).

IR (film): 3054, 2988, 2916, 1647, 1614, 1587, 1495, 1459, 1436, 1383, 1369, 1333, 1311, 1284, 1241, 1200, 1159, 1100, 997, 910, 843, 800, 741, 692, 534, 493, 427 cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 3.04–3.11 (m, 2 H, CH_2P), 4.58–4.65 (m, 2 H, CH_2N), 6.85 and 6.87 (s, 2 H, H-5,6, imidazole), 7.31–7.36 and 7.64–7.70 (m, 11 H, H-4, imidazole, Ph), 7.72 and 7.92 (s, 2 H, H-7,2, imidazole).

^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 32.23 (d, $^1J_{P-C}$ = 48.7 Hz, CH_2P), 40.14 (CH_2N), 109.62 (C-7, imidazole), 120.13 (C-4, imidazole), 122.56 (C-6, imidazole), 123.24 (C-5, imidazole), 128.75 (d,

$^{2}J_{P-C}$ = 12.4 Hz, *o*-C, Ph), 130.27 (d, $^{1}J_{P-C}$ = 79.8 Hz, *i*-C, Ph), 131.21 (d, $^{3}J_{P-C}$ = 10.9 Hz, *m*-C, Ph), 131.94 (d, $^{4}J_{P-C}$ = 2.5 Hz, *p*-C, Ph), 132.82, 142.73 and 142.92 (C-8, 2, 9, imidazole).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 30.69, (s + d satellites, $^{1}J_{P-Se}$ = 738 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –357.1 (d, $^{1}J_{P-Se}$ = 738 Hz).

Anal. Calcd for $C_{21}H_{19}N_2PSe$: C, 61.62; H, 4.68; N, 6.84; P, 7.57; Se, 19.29. Found: C, 61.56; H, 4.66; N, 6.81; P, 7.53; Se, 19.21.

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