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Cross-coupling between secondary phosphine selenides and primary or secondary amines: halogen-free synthesis of phosphinoselenoic amides

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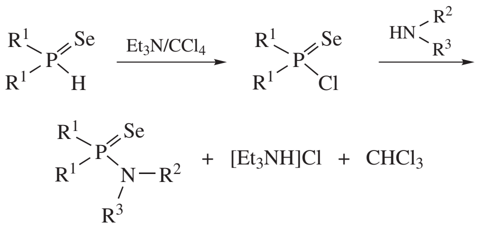
Secondary phosphine selenides react with primary or secondary amines at 60–65 °C in dioxane to give phosphinoselenoic amides.

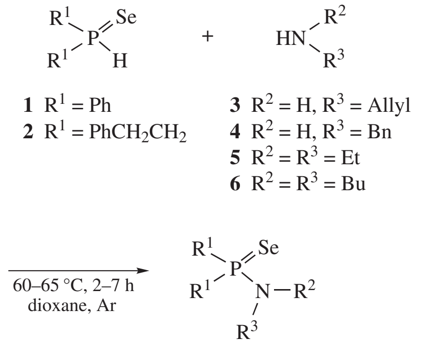
The chemistry of phosphinoselenoic amides has been developed very intensely in the recent decade.[1] Of special interest are organometallic complexes with phosphinoselenoic amide ligands.[2] For example, their complexes with yttrium catalyzes intramolecular alkene hydroamination,[2(a)] whereas the ruthenium complexes act as precatalysts for the transfer hydrogenation of acetophenone.[2(b)] Complexes of phosphinoselenoic amides with transition metals (Ti, Cr, Mn, Fe, Co, Ni, Zn, Cd)[3] are successfully used as single-source precursors of remarkable nanomaterials.[3(c),(d)] Phosphinoselenoic amides are also prospective intermediates for pharmaceuticals.[1(a),(e)] In general, phosphinoselenoic amides are prepared from chemically aggressive phosphorus halides, amines or alkali metal organylamides.[1(a)–(i),3(a),4] Recently a new approach to phosphinoselenoic amides based on the oxidative cross-coupling between secondary phosphine selenides and NH-amines in the Et_3N/CCl_4 system has been published (Scheme 1),[1(j)] triethylammonium chloride and chloroform being formed as the by-products. Apart from these, diorganylphosphinoselenoic chlorides have been identified in the reaction mixture.[1(j)]



Scheme 1

Herein, we report for the first time on unexpected halogen-free version of cross-coupling reaction between secondary phosphine selenides and NH-amines.

We have found that secondary phosphine selenides **1**, **2** react with primary (**3**, **4**) or secondary (**5**, **6**) amines in an equimolar ratio at 60–65 °C for 2–7 h in dioxane under argon to afford diphenyl- and diphenethylphosphinoselenoic amides **7a**–**f** in 25–44% isolated yields[†] (Scheme 2, Table 1, entries 1–6).



1 $R^1 = Ph$
2 $R^1 = PhCH_2CH_2$

3 $R^2 = H$, $R^3 = Allyl$
4 $R^2 = H$, $R^3 = Bn$
5 $R^2 = R^3 = Et$
6 $R^2 = R^3 = Bu$

7a $R^1 = Ph$, $R^2 = H$, $R^3 = Allyl$
7b $R^1 = Ph$, $R^2 = H$, $R^3 = Bn$
7c $R^1 = Ph$, $R^2 = R^3 = Et$
7d $R^1 = Ph$, $R^2 = R^3 = Bu$
7e $R^1 = PhCH_2CH_2$, $R^2 = H$, $R^3 = Allyl$
7f $R^1 = PhCH_2CH_2$, $R^2 = H$, $R^3 = Bn$

Scheme 2

Table 1 Reaction of secondary phosphine selenides with primary or secondary amines (dioxane, 60–65 °C).

Entry	Phosphine selenide	Amine	*t*/h	Amide	Isolated yield (%)
1	**1**	**3**	2	**7a**	33
2	**1**	**4**	4	**7b**	25
3	**1**	**5**	2	**7c**	28
4	**1**	**6**	2	**7d**	27
5	**2**	**3**	2	**7e**	44
6	**2**	**4**	7	**7f**	36
7[a]	**2**	**4**	7	**7f**	36
8[b]	**2**	**3**	9	**7e**	10

[a] Experiment was carried out at 90–95 °C. [b] Benzene was used instead of dioxane.

[†] *Synthesis of compounds* **7** *(general procedure)*. All operations were performed in the laboratory fume hood. A solution of secondary phosphine selenide **1**, **2** (0.4 mmol) and amine **3**–**6** (0.4 mmol) in 2 ml of dioxane was blown with argon and stirred at 60–65 °C for 2–7 h. The reaction was monitored by ^{31}P NMR up to disappearance of peaks of the initial compounds **1**, **2** (3–8 ppm). Along with the target amides **7**, the reaction mixtures contained corresponding secondary phosphines **8**, ammonium phosphinodiselenoates **9** and phosphinoselenoates **10**. After isolation (see below) pure phosphinoselenoic amides **7** were obtained as solids or oils.

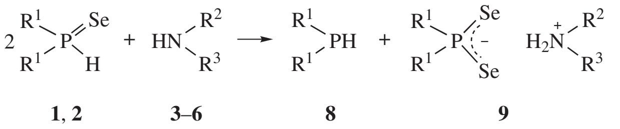
The ^1H, ^{13}C, ^{15}N, ^{31}P and ^{77}Se NMR spectra were recorded on Bruker DPX-400 and AV-400 spectrometers (400.13, 100.62, 40.55, 161.98 and 76.31 MHz, respectively). Chemical shifts ^{15}N of the compounds were determined to within 0.1 ppm using 2D ^1H-^{15}N NMR HMBC technique.

N-*Allyl(diphenyl)phosphinoselenoic amide* **7a**. Dioxane was removed under reduced pressure, the residue was dissolved in 2 ml of benzene and the solution was passed through a layer of Al_2O_3 (0.8 cm, benzene as

An attempt to raise the yields of amides **7** by increasing the reaction temperature up to 90–95 °C gave no desirable results (Table 1, *cf.* entries 6 and 7). The application of benzene as a solvent (instead of dioxane) decreases dramatically the efficacy of the process (Table 1, *cf.* entries 5 and 8).

Note that corresponding secondary phosphines **8** (–70 to –40 ppm, $^1J_{\mathrm{PH}}$ ~ 200 Hz), ammonium phosphinodiselenoates **9** (22–25 ppm, $^1J_{\mathrm{PSe}}$ ~ 560–610 Hz) as well as ammonium phosphinoselenoates[‡] **10** (50–65 ppm, $^1J_{\mathrm{PSe}}$ ~ 635–675 Hz) are also identified in the reaction mixture (^{31}P NMR data). The latter result probably from partial oxidation of the phosphine selenides **1**, **2** to phosphinoselenoic acids followed by their reaction with amines **3–6**. This fact was proved by the increasing the content of phosphinoselenoates **10** in the reaction mixture when reaction proceeded on contact with air.

Compounds **8** and **9** are formed obviously by the direct interaction of the initial reactants **1**, **2** and **3–6** (Scheme 3).



Scheme 3

Such reaction was reported for bis(2-phenylethyl)phosphine selenide and diisopropylamine, which react in the molar ratio of 2:1 at room temperature for 10 min to afford the corresponding ammonium phosphinodiselenoate and bis(2-phenylethyl)phosphine.[5]

We assume that under the conditions elaborated (Table 1), the initially formed ammonium phosphinodiselenoates **9** decompose at heating (60–65 °C) to deliver amides **7** and H_2Se. This assumption has been experimentally proved on the example of phosphinodiselenoate **9e** (synthesized according to published protocol[6]), which, when heated (60–65 °C, 2 h, dioxane), gives amide **7e** almost quantitatively.

Thus, formation of phosphinoselenoic amides **7** proceeds probably *via* reaction of secondary phosphine selenides **1**, **2** and amines **3–6** at room temperature resulting in secondary phosphines **8** and ammonium phosphinodiselenoates **9**. The latter then decompose at heating to amides **7** and hydrogen selenide. Such direction is possible as exemplified by the decomposition of ammonium phenylphosphonamidodiselenoates (toluene, reflux, 12 h) to phenylphosphonoselenoic diamides with releasing of hydrogen selenide.[1(*k*)]

In conclusion, cross-coupling reaction between secondary phosphine selenides and NH-amines represents a novel convenient halogen-free approach to phosphinoselenoic amides, prospective ligands for metal complex catalysts, single-source precursors of nanomaterials and intermediates for pharmaceuticals.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2013.09.004.

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eluent). Benzene was removed and the product was dried *in vacuo*. Yield 0.042 g (33%), yellowish oil. ^{1}H NMR ($CDCl_3$) δ: 2.34 (br. s, 1H, NH), 3.51 (dddt, 2H, CH_2N, $^3J_{\mathrm{HP}}$ 7.5 Hz, $^3J_{\mathrm{HCNH}}$ 7.1 Hz, $^3J_{\mathrm{HCCH}}$ 7.1 Hz, ^4J 1.5 Hz), 5.11 (br. d, 1H$_{cis}$, =CH_2, $^3J_{cis}$ 10.4 Hz), 5.24 (ddt, 1H$_{trans}$, =CH_2, $^3J_{trans}$ 17.1 Hz, $^2J_{\mathrm{HH}}$ 1.5 Hz, $^4J_{\mathrm{HH}}$ 1.5 Hz), 5.93 (ddt, 1H, =CH, $^3J_{trans}$ 17.1 Hz, $^3J_{cis}$ 10.4 Hz, $^3J_{\mathrm{HH}}$ 7.1 Hz), 7.42 (m, 6H, *m*-H$_{\mathrm{Ph}}$, *p*-H$_{\mathrm{Ph}}$), 7.97 (m, 4H, *o*-H$_{\mathrm{Ph}}$). ^{13}C NMR ($CDCl_3$) δ: 44.85 (CH_2N), 116.46 (=CH_2), 128.43 (d, *o*-C$_{\mathrm{Ph}}$, $^2J_{\mathrm{CP}}$ 13.4 Hz), 131.72 (d, *m*-C$_{\mathrm{Ph}}$, $^3J_{\mathrm{CP}}$ 11.2 Hz), 131.83 (d, =CH, $^3J_{\mathrm{CP}}$ 3.0 Hz), 132.64 (d, *p*-C$_{\mathrm{Ph}}$, $^4J_{\mathrm{CP}}$ 11.2 Hz), 133.97 (d, *i*-C$_{\mathrm{Ph}}$, $^1J_{\mathrm{CP}}$ 91.4 Hz). ^{31}P NMR ($CDCl_3$) δ: 58.4 (s + d satellite, $^1J_{\mathrm{PSe}}$ 754.9 Hz). ^{77}Se NMR ($CDCl_3$) δ: –266.4 (d, $^1J_{\mathrm{SeP}}$ 755.3 Hz). Found (%): C, 56.52; H, 4.97; N, 4.19; P, 9.39; Se, 24.92. Calc. for $C_{15}H_{16}NPSe$ (%): C, 56.26; H, 5.04; N, 4.37; P, 9.67; Se, 24.66.

N,N-*Diethyl(diphenyl)phosphinoselenoic amide* **7c**. Dioxane solution was decanted from a precipitate of ammonium phosphinoselenoate **10c**[‡] formed during the reaction. The precipitate was washed with dioxane (2×0.3 ml) and the product was isolated from combined dioxane solution as mentioned for the product **7a**. Yield 0.038 g (28%), white solid, mp 75–76 °C (lit.,[1(*e*)] 77–78 °C). ^{1}H NMR ($CDCl_3$) δ: 1.11 (t, 6H, Me, $^3J_{\mathrm{HH}}$ 7.1 Hz), 3.02 (dq, 4H, CH_2, $^3J_{\mathrm{HP}}$ 12.4 Hz, $^3J_{\mathrm{HH}}$ 7.2 Hz), 7.47 (m, 6H, *m*-H$_{\mathrm{Ph}}$, *p*-H$_{\mathrm{Ph}}$), 8.01 (m, 4H, *o*-H$_{\mathrm{Ph}}$). ^{13}C NMR ($CDCl_3$) δ: 13.54 (d, Me, $^3J_{\mathrm{CP}}$ 5.8 Hz), 41.33 (d, CH_2, $^2J_{\mathrm{CP}}$ 3.4 Hz), 128.33 (d, *m*-C$_{\mathrm{Ph}}$, $^3J_{\mathrm{CP}}$ 12.7 Hz), 131.63 (d, *p*-C$_{\mathrm{Ph}}$, $^4J_{\mathrm{CP}}$ 2.9 Hz), 132.39 (d, *o*-C$_{\mathrm{Ph}}$, $^2J_{\mathrm{CP}}$ 11.0 Hz), 133.26 (d, *i*-C$_{\mathrm{Ph}}$, $^1J_{\mathrm{CP}}$ 92.5 Hz). ^{31}P NMR ($CDCl_3$) δ: 68.2 (s + d satellite, $^1J_{\mathrm{PSe}}$ 746.9 Hz). ^{77}Se NMR ($CDCl_3$) δ: –276.5 (d, $^1J_{\mathrm{SeP}}$ 747.3 Hz). ^{15}N NMR, δ: –334.5. Found (%): C, 57.40; H, 5.81; N, 3.99; P, 8.97; Se, 23.22. Calc. for $C_{16}H_{20}NPSe$ (%): C, 57.15; H, 5.99; N, 4.17; P, 9.21; Se, 23.48.

[‡] *Diethylammonium diphenylphosphinoselenoate* **10c**. Yield 0.013 g (9%), white solid, mp 147–150 °C (decomp.). ^{1}H NMR ($CDCl_3$) δ: 1.21 (t, 6H, Me, $^3J_{\mathrm{HH}}$ 7.5 Hz), 2.74 (q, 4H, CH_2, $^3J_{\mathrm{HH}}$ 7.5 Hz), 7.32 (m, 6H, *m*-H$_{\mathrm{Ph}}$, *p*-H$_{\mathrm{Ph}}$), 7.85 (m, 4H, *o*-H$_{\mathrm{Ph}}$), 9.47 (br. s, 2H, NH_2). ^{13}C NMR ($CDCl_3$) δ: 11.44 (Me), 42.18 (CH_2), 127.81 (d, *m*-C$_{\mathrm{Ph}}$, $^3J_{\mathrm{CP}}$ 12.3 Hz), 129.99 (d, *p*-C$_{\mathrm{Ph}}$, $^4J_{\mathrm{CP}}$ 2.9 Hz), 130.41 (d, *o*-C$_{\mathrm{Ph}}$, $^2J_{\mathrm{CP}}$ 11.1 Hz), 142.61 (d, *i*-C$_{\mathrm{Ph}}$, $^1J_{\mathrm{CP}}$ 91.9 Hz). ^{31}P NMR ($CDCl_3$) δ: 53.68 (s + d satellite, $^1J_{\mathrm{PSe}}$ 650.5 Hz). ^{77}Se NMR ($CDCl_3$) δ: –140.3 (d, $^1J_{\mathrm{SeP}}$ 650.5 Hz). ^{15}N NMR, δ: –328.8. Found (%): C, 53.88; H, 6.21; N, 3.91; P, 9.08; Se, 21.98. Calc. for $C_{16}H_{22}NOPSe$ (%): C, 54.24; H, 6.26; N, 3.95; P, 8.74; Se, 22.29.

For characteristics of compounds **7b**,**d–f** and **10d**, see Online Supplementary Materials.