# Electron-donating ability of triarylphosphines and related compounds studied by $^{31}$P NMR spectroscopy

*M. N. Chevykalova,[a,b]★ L. F. Manzhukova,[c] N. V. Artemova,[b] Yu. N. Luzikov,[a] I. E. Nifant´ev,[a] and E. E. Nifant´ev[b]*

[a]*Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory, 119992 Moscow, Russian Federation. Fax: +7 (095) 939 4523. E-mail: inif@org.chem.msu.ru*
[b]*Department of Chemistry, V. I. Lenin Moscow Pedagogical State University, 3 Nesvizhskii per., 119021 Moscow, Russian Federation. Fax: +7 (095) 246 7766, 248 0162. E-mail: chemfak@centro.ru*
[c]*Department of Chemistry, Chelyabinsk State Pedagogical University, 454080 Chelyabinsk, 69, Russian Federation. Fax: +7 (351 2) 36 7753. E-mail: cs@spi.urc.ac.ru*

The influence of aryl, heterocyclic, amide, alkyl, alkoxyl, thioalkoxyl, and ferrocenyl substituents at the phosphorus atom on its electron-donating ability was studied by the measurement of direct $^{31}$P—$^{77}$Se spin-spin coupling constants for the corresponding selenides. Series of diphenylorganylphosphines and their selenides were studied.

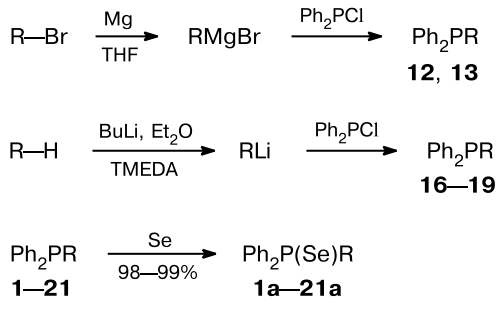
**Key words:** phosphineselenides, $^{31}$P—$^{77}$Se spin-spin coupling constants, heteroarylphosphines.

Tertiary phosphines are widely used for preparation of transition metal complexes employed as catalysts in homogeneous catalysis. The influence of phosphine ligands on the properties and reactivity of metal complexes was established to be mainly determined by electronic and steric effects. Several reviews[1—3] are devoted to the influence of steric factors, whereas electronic effects are poorly studied. To estimate the electron-donating ability of phosphine ligands, researchers use frequencies of stretching vibrations ν(CO) of coordinated CO in monosubstituted transition metal carbonylphosphines,[4,5] direct $^{31}$P—$^{195}$Pt spin-spin coupling constants (SSC) of the platinum phosphine complexes,[6,7] and direct $^{31}$P—$^{77}$Se SSC constants of the corresponding selenephosphines.[6] In our opinion, the latter is most available among the listed approaches.

According to the studies,[6] the $^1J_{P,Se}$ values for selenides depend on the nature of substituents at the P atom: electron-withdrawing groups increase and electron-donating groups decrease this parameter. Note that these regularities were observed[6] for the restricted number of phosphine samples. Since search for new ligands is an urgent problem, it seemed of interest to extend the scope of studied organophosphorus compounds and to study more specifically how the substituent nature affects a change in the electron-donating ability of the P atom (Table 1).

We synthesized a group of compounds related to $Ph_3P$, whose molecules contained the heterocyclic, aryl, alkyl, ferrocenyl, amido, alkoxy, or thio fragment instead of one Ph group. The indole, imidazole, or thiophene residues were used as heterocyclic substituents. Diphenylorganylphosphines **12**, **13**, and **16—19** were synthesized by the reactions of the corresponding magnesium or lithium salts with $Ph_2PCl$. On boiling with selenium in chloroform,[6] compounds **12**, **13**, and **16—19** were transformed into the corresponding selenides (Scheme 1).

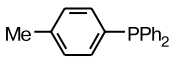
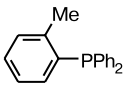
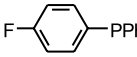
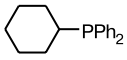
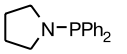
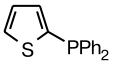
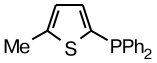
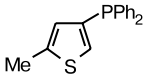
**Scheme 1**

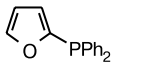
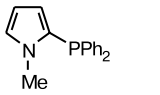
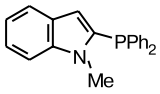
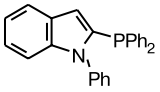
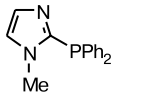
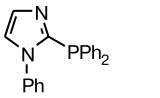
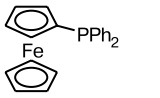
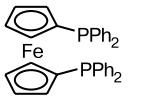



| Compound | R | Yield (%) |
|---|---|---|
| **12** | 2-Methyl-5-thienyl | 92 |
| **13** | 2-Methyl-4-thienyl | 61 |
| **16** | *N*-Methylindolyl | 74 |
| **17** | *N*-Phenylindolyl | 54 |
| **18** | *N*-Methylimidazolyl | 33 |
| **19** | *N*-Phenylimidazolyl | 27 |

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 75—80, January, 2003.

**Table 1.** $^{31}P$ NMR spectroscopic data for organophosphorus compounds $Ph_2PR$ **1—21** and their selenides $Ph_2P(Se)R$ **1a—21a** ($CDCl_3$)

| $Ph_2PR$ | | δ | | $^1J_{P,Se}$ | $\Delta^1J_{P,Se}$[a] |
|---|---|---|---|---|---|
| | | $Ph_2PR$ | $Ph_2P(Se)R$ | Hz | |
| $Ph_3P$ (**1**) | | −8.0<br>−4.7 [b]<br>−8.0 [c] | 32.6<br>35.9 [b] | 730<br>732 [b] | — |
|  | (**2**) | −8.8 | 32.1 | 726 | −4 |
|  | (**3**) | −13 [b] | 32.6 [b] | 730 [b] | 0 |
|  | (**4**) | −9.3 | 31.6 | 734 | 4 |
| $Bu^tPPh_2$ (**5**) | | −43.1 | 54.0 | 717 | −13 |
|  | (**6**) | −6.3 | 42.8 | 726 | −4 |
| $Ph_2PNEt_2$ (**7**) | | 59.0 | 64.6 | 747 | 17 |
|  | (**8**) | 44.8 [d] | 63.7 | 748 | 18 |
| $Bu^tSPPh_2$ (**9**) | | — | 39.2 | 772 | 42 |
| $Ph_2POEt$ (**10**) | | 108.4 | 81.7 | 796 | 66 |
|  | (**11**) | −19.3 [b] | 20.6 [b] | 743 [b] | 13 |
|  | (**12**) | −21.9 | 19.3 | 733 | 3 |
|  | (**13**) | −20.2 | 20.3 | 728 | −2 |

| $Ph_2PR$ | | δ, м.д. | | $^1J_{P,Se}$ | $\Delta^1J_{P,Se}$[a] |
|---|---|---|---|---|---|
| | | $Ph_2PR$ | $Ph_2P(Se)R$ | Гц | |
|  | (**14**) | −26.6 [b] | 16.9 [b] | 754 [b] | 24 |
|  | (**15**) | −29.7 [b] | 17.5 [b] | 728 [b] | −2 |
|  | (**16**) | −30.7 | 16.3 | 731 | 1 |
|  | (**17**) | −30.7 | 17.2 | 747 | 17 |
|  | (**18**) | −33.2 | 15.4 | 737 | 7 |
|  | (**19**) | −32.0 | 16.6 | 754 | 24 |
|  | (**20**) | −19.2 | 29.1 | 732 | 2 |
|  | (**21**) | −19.8 | 28.2 | 737 | 7 |

[a] Difference of the $^{31}P—^{77}Se$ SSC constants for $Ph_2P(Se)R$ and $Ph_3PSe$.
[b] See Ref. 6.
[c] See Ref. 8.
[d] $C_6D_6$ is solvent.

Organophosphorus compounds containing ferrocenyl alkyl, amino, alkoxy, or thio group and their selenides were synthesized using standard procedures. The data of $^{31}P$ NMR spectroscopy for the synthesized selenides and published data[6,8] are presented in Table 1.

The influence of a substituent was qualitatively evaluated by comparison of the $^1J_{P,Se}$ values for the studied compounds and $Ph_3P$ (direct $^{31}P—^{77}Se$ SSC constants for all considered compounds are positive). The following conclusions were made.

The introduction of the Me group into both the *ortho*- and *para*-positions of the Ph ring increases the electron-donating ability of phosphine. The appearance of the F atom in the *para*-position of the Ph ring makes the phosphine more electron-withdrawing than $Ph_3P$: $^1J_{P,Se}$ for *p*-$FC_6H_4P(Se)Ph_2$ is 734, and that for $Ph_3PSe$ is 730. However, it should be mentioned that when the benzene ring was modified, the detected changes in the constant turned out small.

The replacement of one Ph group in the $Ph_3P$ molecule by the amido, alkoxy, or thio group enhances the electron-withdrawing ability of the phosphine. The highest constant is observed in the case of alkoxy group introduction, which is due to a higher electronegativity of the O atom than those of N and S. On going from thio- to amidophosphines, $^1J_{P,Se}$ decreases, and the constant value is independent of the amino group structure.

Special attention should be given to the results for phosphines containing the heterocyclic fragment. It has previously been mentioned[9] that ligands containing electron-withdrawing substituents dissociate from the metallic center more easily to favor the acceleration of the catalytic reaction. Among all heteroarylphosphines presented in Table 1, compounds **14** and **19** are most elec-

tron-withdrawing. Phosphines with nitrogen-containing heterocycles are characterized by the following regularities: all nitrogen heteroarylphosphines, except for *N*-methylpyrrole heteroarylphosphine, are less electron-donating than $Ph_3P$; the replacement of the methyl group at the N atom by the phenyl group increases the electron-withdrawing ability of the phosphine (for the indole and imidazole derivatives, the direct $^{31}P—^{77}Se$ SSC constant increases by 16 and 17 Hz, respectively); the electron-withdrawing ability of phosphines decreases in the series imidazolyl > indolyl > pyrrolyl. Comparing heteroarylphosphines containing the thiophene fragment (**11—13**), one can note the following: 3-thienyl groups are less electron-withdrawing than their 2-isomers; introduction of the Me substituent into position 5 of the thiophene ring (compound **12**) makes phosphine less electron-withdrawing, which is reflected as a decrease in $^1J_{P,Se}$ of selenide; diphenylphosphino group in position 3 facilitates thienylphosphine (compound **13**) to become even more electron-donating than $Ph_3P$.

The introduction of the ferrocenyl substituent makes phosphine slightly more electron-withdrawing than $Ph_3P$ ($^1J_{P,Se}$ of selenide **20** differs from the direct constant in $Ph_3PSe$ by 2 Hz only). The appearance of the diphenylphosphino group in the second ring of ferrocene increases $^1J_{P,Se}$ of the corresponding selenide.

The replacement of the Ph group in $Ph_3P$ by a saturated hydrocarbon radical substantially changes the electronic properties of phosphine. For example, the introduction of the *tert*-butyl or cyclohexyl group favors an increase in the electron-donating ability of phosphine, which is reflected as a decrease in the direct $^{31}P—^{77}Se$ SSC constant of selenide. This fact agrees completely with previous results.[6]

Thus, we can conclude that the electron-donating ability of tertiary phosphines can substantially be varied due to a change in heterocyclic radicals in molecules of these compounds.

## Experimental

All experiments were carried out in argon. Solvents were purified as follows[10]: ethereal solvents were stored and distilled over KOH and then over sodium benzophenone ketyl; $CHCl_3$ was washed with water, concentrated $H_2SO_4$, and water to neutral reaction, dried over $CaCl_2$, and distilled over $P_2O_5$; benzene was dried by refluxing and distillation over sodium. Commercial reagents available from Lancaster, Merck, and Fluka were used. $^1H$, $^{31}P$, and $^{13}C$ NMR spectra were recorded on a Varian VXR-400 instrument. For measurements of $\delta_P$ of organophosphorus compounds and their selenides, 70% $H_3PO_4$ was used as external standard (a sealed capillary was immersed in a solution and centered). The measurement of $^1J_{P,Se}$ was carried out at 20 °C (±1—2 °C). The accuracy of measurement of the direct $^{31}P—^{77}Se$ SSC constant was ±0.5 Hz. The reproducibility of results was sufficiently high. The temperature and concentration dependences of $^1J_{P,Se}$ for selenide were not studied. The element composition of all compounds was determined using an automated Carlo—Erba analyzer at the MONTELL Research Center (Ferrara, Italy).

2-Methyl-5-bromothiophene,[11] 2-methyl-4-bromothiophene,[12,13] *N*-methylindole,[14] *N*-phenylindole,[15] and *N*-phenylimidazole[15] were synthesized using known procedures. ***p*-Tolyldiphenylphosphine (2),[16] (4-fluorophenyl)diphenylphosphine (4),[17] *tert*-butyldiphenylphosphine (5),[18] cyclohexyldiphenylphosphine (6),[19] *N*,*N*-diethyl(diphenyl)phosphinamide (7),[20] ethyl(diphenyl) phosphinite (10),[20] ferrocenyldiphenylphosphine (20),[21] and 1,1´-bis(diphenylphosphino)ferrocene (21)[22]** were synthesized using standard methods.

**1-(Diphenylphosphino)pyrrolidine (8)** was synthesized similarly to compound **7** [20] from pyrrolidine (3.8 mL, 0.045 mol), $Et_3N$ (6.3 mL, 0.045 mol), $Et_2O$ (200 mL), and $Ph_2PCl$ (8.1 mL, 0.045 mol). The product was obtained in 48% yield (5.53 g) as a colorless liquid, b.p. 142 °C (0.6 Torr). Found (%): C, 75.23; H, 7.21; N, 5.38. $C_{16}H_{18}PN$. Calculated (%): C, 75.27; H, 7.11; N, 5.49. $^1H$ NMR ($C_6D_6$), δ: 2.50—2.60, 3.00—3.10 (both m, 4 H each, $CH_2$); 7.15—7.30 (m, 6 H, CH=, Ph); 7.50—7.60 (m, 4 H, CH=, Ph).

***tert*-Butylthio(diphenyl)phosphine (9)** was synthesized similarly to compound **7** [20] from $HSBu^t$ (5.1 mL, 0.045 mol), $Et_3N$ (6.3 mL, 0.045 mol), $Et_2O$ (200 mL), and $Ph_2PCl$ (8.1 mL, 0.045 mol). Due to its easy hydrolyzability and oxidizability, the product was used for the synthesis of selenide without additional purification.

**(2-Methyl-5-thienyl)diphenylphosphine (12).** A solution of $Ph_2PCl$ (3 mL, 0.02 mol) in THF (5 mL) was added on cooling to −40 °C to a solution of 2-methyl-5-thienylmagnesium bromide prepared from Mg (0.45 g, 0.019 mol), dibromoethane (0.15 mL, 0.0017 mol), and 5-bromo-2-methylthiophene (3 g, 0.017 mol) in THF (20 mL). The reaction mixture was stirred for 12 h at ~20 °C, then water was added (10 mL), the organic layer was separated, and the aqueous layer was extracted with $Et_2O$ (3×10 mL). The combined organic fractions were washed with water and dried above $MgSO_4$; the solvents were removed at reduced pressure. The obtained yellow oil was purified by column chromatography (silica gel 60, benzene—AcOEt, 4 : 1). The solvents were removed at reduced pressure. Compound **12** was obtained in 92% yield (4.41 g) as a yellowish oil, which crystallized during prolonged storage, m.p. 49—50 °C. Found (%): C, 72.15; H, 5.41. $C_{17}H_{15}PS$. Calculated (%): C, 72.32; H, 5.35. $^1H$ NMR ($CDCl_3$), δ: 2.55 (s, 3 H, Me); 6.86 (m, 1 H, CH= of thiophene ring; 7.26 (dd, 1 H, CH= of thiophene ring, $J$ = 3.4 Hz, $J$ = 6.7 Hz); 7.40—7.44, 7.47—7.52 (both m, 10 H, Ph).

**(2-Methyl-4-thienyl)diphenylphosphine (13)** was synthesized similarly to compound **12** from Mg (1.49 g, 0.062 mol), dibromoethane (0.5 mL, 0.0057 mol), 4-bromo-2-methylthiophene (10 g, 0.057 mol), THF (70 mL), and $Ph_2PCl$ (12.2 mL, 0.068 mol). The product was obtained in 61% yield (9.73 g) as a yellowish oil. Found (%): C, 72.18; H, 5.19. $C_{17}H_{15}PS$. Calculated (%): C, 72.32; H, 5.35. $^1H$ NMR ($CDCl_3$), δ: 2.55 (d, 3 H, Me, $J$ = 1.1 Hz); 6.79 (m, 1 H, CH= of thiophene ring), 7.09 (dd, 1 H, CH= of thiophene ring, $J$ = 1.4 Hz, $J$ = 4.7 Hz); 7.40—7.51 (m, 10 H, Ph).

**(*N*-Methyl-2-indolyl)diphenylphosphine (16).** A 1.6 *M* solution of $Bu^nLi$ in hexane (11.1 mL, 0.018 mol) was added on cooling to −70 °C to a solution of *N*-methylindole (2.2 g, 0.017 mol) and TMEDA (2.7 mL, 0.018 mol) in $Et_2O$ (15 mL).

The reaction mixture was stirred for 4 h at ~20 °C, cooled to −40 °C, and a solution of $Ph_2PCl$ (3.2 mL, 0.018 mol) in $Et_2O$ (5 mL) was added dropwise. Cooling was stopped, and the reaction mixture was left for stirring for 12 h. Water (10 mL) was added to the mixture, the organic layer was separated, and the aqueous layer was extracted with $Et_2O$ (3×10 mL). The combined organic fractions were washed with water (2×10 mL) and dried above $MgSO_4$; the solvents were removed at reduced pressure. The solid residue was purified by column chromatography (silica gel 60, benzene), and the solvent was evaporated at reduced pressure. The product was obtained in 74% yield (4 g) as a white crystalline substance, m.p. 120—122 °C. Found (%): C, 80.10; H, 5.70; N, 4.36. $C_{21}H_{18}NP$. Calculated (%): C, 79.98; H, 5.75; N, 4.44. $^1$H NMR ($CDCl_3$), δ: 3.70 (s, 3 H, Me); 6.14 (s, 1 H, CH= of indole ring); 7.08 (t, 1 H, CH=, Ar, $J$ = 8.0 Hz); 7.21 (m, 1 H, CH=, Ar); 7.29—7.41 (m, 11 H, CH=, Ar); 7.51 (d, 1 H, CH=, Ar, $J$ = 10.0 Hz).

**(*N*-Phenyl-2-indolyl)diphenylphosphine (17)** was synthesized similarly to compound **16** from *N*-phenylindole (1.34 g, 6.95 mmol), TMEDA (1.1 mL, 7.3 mmol), a 1.6 *M* solution of $Bu^nLi$ in hexane (4.6 mL, 7.3 mmol), $Ph_2PCl$ (1.4 mL, 7.7 mmol), and $Et_2O$ (15 mL). The precipitate, which was formed after water (10 mL) was added to the reaction mixture, was filtered off, washed with water (3×10 mL) and hexane (15 mL), and dried in high vacuum. The product was obtained in 54% (1.42 g) as a white crystalline substance, m.p. 183—184 °C. Found (%): C, 82.83; H, 5.40; N, 3.62. $C_{26}H_{20}NP$. Calculated (%): C, 82.74; H, 5.34; N, 3.71. $^1$H NMR ($CDCl_3$), δ: 6.38 (s, 1 H, CH= of indole ring); 7.16—7.22, 7.26—7.30, 7.36—7.44, 7.60—7.62 (all m, 19 H, CH=, Ar).

**(*N*-Methyl-2-imidazolyl)diphenylphosphine (18).** A 1.6 *M* solution of $Bu^nLi$ in hexane (10 mL, 0.016 mol) was added on cooling to −70 °C to a solution of *N*-methylimidazole (1.25 g, 0.015 mol) and TMEDA (2.4 mL, 0.016 mol) in $Et_2O$ (12 mL). The reaction mixture was stirred for 4 h at ~20 °C, cooled to −40 °C, and added by a solution of $Ph_2PCl$ (2.9 mL, 0.016 mol) in $Et_2O$ (5 mL). Cooling was stopped, the reaction mixture was left for stirring for 12 h, and water (10 mL) was added to the mixture. The organic layer was separated, and the aqueous layer was extracted with $Et_2O$ (3×10 mL). The combined organic fractions were washed with water (2×10 mL) and dried above $MgSO_4$; solvents were removed at reduced pressure. The solid residue was purified by column chromatography (silica gel 60, benzene—AcOEt (4 : 1 — I fraction, 1 : 1 — II fraction)). All solvents were removed under reduced pressure. Fraction II contained compound **18**. The product was obtained in 33% yield (1.36 g) as a white crystalline substance, m.p. 73 °C. Found (%): C, 72.05; H, 5.73; N, 10.39. $C_{16}H_{15}N_2P$. Calculated (%): C, 72.17; H, 5.68; N, 10.52. $^1$H NMR ($CDCl_3$), δ: 3.80 (s, 3 H, Me); 7.11 (m, 1 H, CH= of imidazole ring); 7.35 (br.s, 1 H, CH= of imidazole ring); 7.42—7.46 (m, 6 H, CH=, Ph); 7.53—7.58 (m, 4 H, CH=, Ph).

**(*N*-Phenyl-2-imidazolyl)diphenylphosphine (19)** was synthesized similarly to compound **18** from *N*-phenylimidazole (2 g, 0.014 mol), TMEDA (2.2 mL, 0.015 mol), a 1.6 *M* solution of $Bu^nLi$ in hexane (9.1 mL, 0.015 mol), $Ph_2PCl$ (2.6 mL, 0.015 mol), and $Et_2O$ (25 mL). The precipitate, formed after water (10 mL) was added to the reaction mixture, was filtered off, washed with water (3×10 mL) and $Et_2O$ (20 mL), dried in high vacuum, and purified by column chromatography (silica

**Table 2.** $^{13}$C NMR spectroscopic data for organophosphorus compounds $Ph_2PR$ **8**, **12**, **13**, and **16**—**19** ($CDCl_3$)

| Compound | R | δ ($J$/Hz) | |
|---|---|---|---|
| | | $Ph_2P$ | R |
| **8** | Pyrrolidyl* | 128.36 (CH=, $J$ = 5.7); 128.43, 132.49 (CH=, $J$ = 19.5); 139.96 (=C<, $J$ = 14.3) | 26.46 ($CH_2$, $J$ = 5.3); 49.81 ($CH_2$, $J$ = 13.0) |
| **12** | 2-Methyl-5-thienyl | 128.17 (CH=, $J$ = 7.0); 128.48, 132.78 (CH=, $J$ = 19.4); 138.10 (=C<, $J$ = 8.3) | 15.36 (Me); 126.25 (CH=, $J$ = 8.7); 134.96 (=C<, $J$ = 27.0); 136.83 (CH=, $J$ = 28.9); 147.06 (=C<) |
| **13** | 2-Methyl-4-thienyl | 128.25 (CH=, $J$ = 6.9); 128.45, 133.12 (CH=, $J$ = 19.5); 137.56 (=C<, $J$ = 9.9) | 15.03 (Me); 129.07 (CH=, $J$ = 17.0); 129.52 (CH=, $J$ = 23.1); 136.23 (=C<, $J$ = 13.1); 140.93 (=C<, $J$ = 6.2) |
| **16** | *N*-Methyl-2-indolyl | 128.48 (CH=, $J$ = 7.0); 128.96, 133.59 (CH=, $J$ = 19.8); 135.20 (=C<, $J$ = 6.9) | 31.02 (Me, $J$ = 13.7); 108.99 (CH=, $J$ = 2.0); 110.36 (CH=, $J$ = 2.5); 119.40, 120.46, 121.96 (CH=); 127.80 (=C<, $J$ = 2.5); 136.97 (=C<, $J$ = 3.6); 139.83 (=C<, $J$ = 2.6) |
| **17** | *N*-Phenyl-2-indolyl | 128.29 (CH=, $J$ = 7.3); 128.85 (CH=, $J$ = 2.5); 133.78 (CH=, $J$ = 20.5); 135.75 (=C<, $J$ = 7.5) | 110.40, 111.90, 120.14, 120.41, 122.53, 127.81 (CH=); 127.94 (=C<); 128.26, 128.41 (CH=, $J$ = 2.7); 137.95, 138.46 (=C<, $J$ = 5.3); 140.60 (=C<) |
| **18** | *N*-Methyl-2-imidazolyl | 128.27 (CH=, $J$ = 7.7); 128.81, 133.44 (CH=, $J$ = 20.3); 134.72 (=C<, $J$ = 4.2) | 33.67 (Me, $J$ = 14.2); 123.35, 130.70 (CH=, $J$ = 3.0); 145.54 (=C<) |
| **19** | *N*-Phenyl-2-imidazolyl | 128.26 (CH=, $J$ = 7.6); 128.84, 133.69 (CH=, $J$ = 20.7); 135.43 (=C<, $J$ = 5.3) | 123.60, 126.17 (CH=, $J$ = 3.7); 128.30, 128.84, 131.19 (CH=); 137.78, 146.52 (=C<, $J$ = 7.0) |

* $C_6D_6$ was used as the solvent.

gel 60, benzene—AcOEt, 1 : 1). The solvents were removed at reduced pressure. The product was obtained in 27% (1.25 g) as a white finely crystalline substance, m.p. 124—125 °C. Found (%): C, 76.92; H, 5.84; N, 8.42. $C_{21}H_{17}N_2P$. Calculated (%): C, 76.82; H, 5.22; N, 8.53. $^1$H NMR ($CDCl_3$), δ: 7.28—7.31, 7.32—7.33, 7.38—7.42, 7.43—7.47, 7.50—7.56 (all m, 17 H, CH= of imidazole ring, Ph).

The $^{13}$C NMR spectra of the above organophosphorus compounds are presented in Table 2.

**Synthesis of selenides** was carried out using a known procedure.[6] A solution of an organophosphorus compound (0.001 mol) in $CHCl_3$ (for **1**, **2**, **4**—**6**, **12**, **13**, and **16**—**21**) or in benzene (for **7**—**10**) was boiled with selenium (0.3 g, 3.8 mmol) for 5 h. A selenium excess was filtered off, and the solvent was removed at reduced pressure. The yields were 98—99%. The characteristics of the synthesized selenides are presented below.

**Selenide 2a.** White crystalline substance, m.p. 150 °C. Found (%): C, 64.14; H, 4.89. $C_{19}H_{17}PSe$. Calculated (%): C, 64.23; H, 4.82. $^1$H NMR ($CDCl_3$), δ: 2.44 (s, 3 H, Me); 7.29 (dd, 2 H, CH=, Ar, $J$ = 2.8 Hz, $J$ = 8.4 Hz); 7.44—7.55 (m, 6 H, CH=, Ar); 7.62—7.69 (dd, 2 H, CH=, Ar, $J$ = 8.0 Hz, $J$ = 13.5 Hz); 7.73—7.80 (dd, 4 H, CH=, Ar, $J$ = 7.5 Hz, $J$ = 13.6 Hz).

**Selenide 4a.** White crystalline substance, m.p. 137—139 °C. Found (%): C, 60.24; H, 4.02. $C_{18}H_{14}FPSe$. Calculated (%): C, 60.18; H, 3.93. $^1$H NMR ($CDCl_3$), δ: 7.14—7.20 (td, 2 H, CH=, Ar, $J$ = 4.0 Hz, $J$ = 10.0 Hz); 7.46—7.58 (m, 6 H, CH=, Ar); 7.72—7.82 (m, 6 H, CH=, Ar).

**Selenide 5a.** The product was purified by column chromatography (silica gel 60, benzene). Light yellow crystalline substance, m.p. 66 °C. Found (%): C, 59.71; H, 6.09. $C_{16}H_{19}PSe$. Calculated (%): C, 59.82; H, 5.96. $^1$H NMR ($CDCl_3$), δ: 2.40 (d, 9 H, Me, $J$ = 17 Hz); 7.45—7.55 (m, 6 H, CH=, Ph); 8.01—8.08 (m, 4 H, CH=, Ph).

**Selenide 6a.** White crystalline substance, m.p. 138—139 °C. Found (%): C, 62.39; H, 6.04. $C_{18}H_{21}PSe$. Calculated (%): C, 62.25; H, 6.09. $^1$H NMR ($CDCl_3$), δ: 1.20—1.40 (m, 3 H, *cyclo*-$C_6H_{11}$); 1.60—1.80 (m, 5 H, *cyclo*-$C_6H_{11}$); 1.80—1.90 (m, 2 H, $CH_2$, *cyclo*-$C_6H_{11}$); 2.60—2.70 (m, 1 H, CH<, *cyclo*-$C_6H_{11}$); 7.40—7.60 (m, 6 H, CH=, Ph); 7.90—8.10 (m, 4 H, CH=, Ph).

**Selenide 7a.** White crystalline substance, m.p. 88—89 °C. Found (%): C, 57.02; H, 5.95; N, 4.28. $C_{16}H_{20}NPSe$. Calculated (%): C, 57.15; H, 5.99; N, 4.17. $^1$H NMR ($CDCl_3$), δ: 1.15 (t, 6 H, Me, $J$ = 9.2 Hz); 3.04—3.13 (qd, 4 H, $CH_2$, $J$ = 12.3 Hz, $J$ = ~1 Hz); 7.46—7.54 (m, 6 H, CH=, Ph); 8.04—8.12 (m, 4 H, CH=, Ph).

**Selenide 8a.** White crystalline substance, m.p. 137—139 °C. Found (%): C, 57.54; H, 5.57; N, 4.09. $C_{16}H_{18}NPSe$. Calculated (%): C, 57.49; H, 5.43; N, 4.19. $^1$H NMR ($CDCl_3$), δ: 1.90—2.00, 2.95—3.05 (both m, 4 H each, $CH_2$); 7.44—7.52 (m, 6 H, CH=, Ph); 8.11—8.18 (m, 4 H, CH=, Ph).

**Selenide 9a.** The product was purified by column chromatography (silica gel 60, benzene). Orange crystalline substance, m.p. 73—75 °C. Found (%): C, 54.43; H, 5.51. $C_{16}H_{19}PSSe$. Calculated (%): C, 54.39; H, 5.42. $^1$H NMR ($CDCl_3$), δ: 1.60 (s, 9 H, Me); 7.45—7.55 (m, 6 H, CH=, Ph); 8.05—8.15 (m, 4 H, CH=, Ph).

**Selenide 10a.** Colorless oil. Found (%): C, 54.29; H, 4.95; O, 5.01. $C_{14}H_{15}OPSe$. Calculated (%): C, 54.38; H, 4.89; O, 5.17. $^1$H NMR ($CDCl_3$), δ: 1.90 (t, 3 H, Me, $J$ = 7.1 Hz); 4.13—4.21 (qd, 2 H, $CH_2$, $J$ = 9.1 Hz, $J \approx$ 1 Hz); 7.46—7.56 (m, 6 H, CH=, Ph); 7.92—7.99 (m, 4 H, CH=, Ph).

**Selenide 12a.** White crystalline substance, m.p. 128 °C. Found (%): C, 56.61; H, 4.12. $C_{17}H_{15}PSSe$. Calculated (%): C, 56.51; H, 4.18. $^1$H NMR ($CDCl_3$), δ: 2.56 (s, 3 H, Me); 6.90 (m, 1 H, CH= of thiophene ring); 7.32 (dd, 1 H, CH= of thiophene ring, $J$ = 3.7 Hz, $J$ = 8.8 Hz); 7.46—7.58 (m, 6 H, CH=, Ph); 7.80—7.86 (m, 4 H, CH=, Ph).

**Selenide 13a.** White crystalline substance, m.p. 161 °C. Found (%): C, 56.64; H, 4.21. $C_{17}H_{15}PSSe$. Calculated (%): C, 56.51; H, 4.18. $^1$H NMR ($CDCl_3$), δ: 2.51 (s, 3 H, Me); 7.02 (d, 1 H, CH= of thiophene ring, $J$ = 3.6 Hz); 7.42 (d, 1 H, CH= of thiophene ring, $J$ = 9.1 Hz); 7.46—7.56 (m, 6 H, CH=, Ph); 7.76—7.84 (dd, 4 H, CH=, Ph, $J$ = 8.0 Hz, $J$ = 16.0 Hz).

**Selenide 16a.** White crystalline substance, m.p. 176 °C. Found (%): C, 64.05; H, 4.51; N, 3.69. $C_{21}H_{18}NPSe$. Calculated (%): C, 63.97; H, 4.60; N, 3.55. $^1$H NMR ($CDCl_3$), δ: 3.93 (s, 3 H, Me); 6.28 (d, 1 H, CH= of indole ring, $J$ = 4.7 Hz); 7.20 (t, 1 H, CH=, Ar, $J$ = 8.0 Hz); 7.36—7.44 (m, 2 H, CH=, Ar); 7.52—7.64 (m, 7 H, CH=, Ar); 7.90—7.98 (m, 4 H, CH=, Ar).

**Table 3.** $^{13}$C NMR spectroscopic data for selenides $Ph_2P(Se)R$ **2a**, **4a**, **5a**—**10a**, **12a**, **13a**, and **16a**—**21a** ($CDCl_3$)

| Compound | R | δ ($J$/Hz) | |
|---|---|---|---|
| | | $Ph_2P(Se)$ | R |
| **2a** | *p*-Tolyl | 128.30 (CH=, $J$ = 12.7); 131.32 ($J$ = 2.9); 131.91 (=C<, $J$ = 77.0); 132.41 (CH=, $J$ = 10.7) | 21.29 (Me); 128.10 (=C<, $J$ = 79.0); 129.12 (CH=, $J$ = 13.0); 132.53 (CH=, $J$ = 10.8); 142.02 (=C<, $J$ = 3.0) |
| **4a** | 4-Fluorophenyl | 128.42 (CH=, $J$ = 12.7); 131.47 (=C<, $J$ = 77.5); 131.53 (CH=, $J$ = 2.8); 132.32 (CH=, $J$ = 10.7) | 115.59 (dd, CH=, $J$ = 13.9, $J$ = 21.7); 127.50 (dd, =C<, $J$ = 2.9, $J$ = 79.4); 134.92 (dd, CH=, $J$ = 8.8, $J$ = 12.6); 164.58 (dd, =C<, $J$ = 3.2, $J$ = 254.1) |
| **5a** | *tert*-Butyl | 127.90 (CH=, $J$ = 11.3); 129.79 (=C<, $J$ = 65.6); 131.00 (CH=, $J$ = 2.6); 133.25 (CH=, $J$ = 9.1) | 26.42 (Me); 35.43 (>C<, $J$ = 42.1) |
| **6a** | Cyclohexyl | 128.28 (CH=, $J$ = 11.5); 129.96 (=C<, $J$ = 68.7); 131.11 (CH=, $J$ = 2.6); 131.88 (CH=, $J$ = 9.7) | 25.42, 25.79, 25.96 ($CH_2$); 37.46 (>CH, $J$ = 48.0) |

(*to be continued*)

**Table 3** (*continued*)

| Compound | R | δ (*J*/Hz) | |
|---|---|---|---|
| | | $Ph_2P(Se)$ | R |
| **7a** | Diethylamino | 128.04 (CH=, *J* = 12.7); 131.35 (CH=, *J* = 2.9); 132.09 (CH=, *J* = 11.0); 132.98 (=C<, *J* = 92.3) | 13.27 (*J* = 5.9) (Me); 41.04 ($CH_2$, *J* = 3.1) |
| **8a** | Pyrrolidyl | 128.08 (CH=, *J* = 12.6); 131.41 (CH=, *J* = 2.9); 131.99 (CH=, *J* = 11.0); 132.85 (=C<, *J* = 93.4) | 25.88 ($CH_2$, *J* = 8.1); 47.65 ($CH_2$, *J* = 2.1) |
| **9a** | *tert*-Butylthio | 128.12 (CH=, *J* = 13.2); 131.36 (CH=, *J* = 3.2); 131.79 (CH=, *J* = 11.2); 134.20 (=C<, *J* = 74.1) | 32.22 (*J* = 4.3) (Me); 53.79 (>C<, *J* = 4.0) |
| **10a** | Ethoxy | 128.07 (CH=, *J* = 13.5); 130.89 (CH=, *J* = 11.9); 131.57 (CH=, *J* = 2.5); 134.57 (=C<, *J* = 98.2) | 15.80 (*J* = 8.4) (Me); 61.99 ($CH_2$, *J* = 5.3) |
| **12a** | 2-Methyl-5-thienyl | 128.28 (CH=, *J* = 13.0); 131.50 (CH=, *J* = 2.9); 131.91 (CH=, *J* = 11.5); 132.56 (=C<, *J* = 80.8) | 15.41 (Me); 126.81 (CH=, *J* = 13.1); 130.54 (=C<, *J* = 86.6); 137.94 (CH=, *J* = 9.2); 150.17 (=C<, *J* = 4.2) |
| **13a** | 2-Methyl-4-thienyl | 128.31 (CH=, *J* = 12.8); 131.41 (CH=, *J* = 2.7); 131.93 (=C<, *J* = 78.6); 132.01 (CH=, *J* = 11.1) | 15.09 (Me); 127.52 (CH=, *J* = 15.3); 132.05 (=C<, *J* = 80.5); 133.23 (CH=, *J* = 13.7); 142.46 (=C<, *J* = 14.7) |
| **16a** | *N*-Methyl-2-indolyl | 128.44 (CH=, *J* = 13.0); 130.37 (=C<, *J* = 80.3); 131.82 (CH=, *J* = 2.9); 132.48 (CH=, *J* = 11.4) | 32.35 (Me); 109.59, 113.76 (CH=, *J* = 13.7); 120.26, 121.56, 124.15 (CH=); 125.98 (=C<, *J* = 12.6); 127.91 (=C<, *J* = 92.2); 141.08 (=C<, *J* = 7.4) |
| **17a** | *N*-Phenyl-2-indolyl | 128.27 (CH=, *J* = 7.9); 130.67 (=C<, *J* = 80.8); 131.53 (CH=, *J* = 2.8); 132.76 (CH=, *J* = 11.1) | 111.03, 115.67 (CH=, *J* = 13.7); 120.90, 121.37, 124.59 (CH=); 125.82 (=C<, *J* = 12.4); 128.10, 128.23 (CH=); 129.49 (=C<, *J* = 93.7); 129.67 (CH=); 136.71, 142.42 (=C<, *J* = 6.6) |
| **18a** | *N*-Methyl-2-imidazolyl | 128.35 (CH=, *J* = 13.2); 130.01 (=C<, *J* = 81.8); 131.81 (CH=, *J* = 3.0); 132.31 (CH=, *J* = 11.4) | 35.55 (Me); 126.44, 129.72 (CH=, *J* = 16.1); 137.57 (=C<, *J* = 124.6) |
| **19a** | *N*-Phenyl-2-imidazolyl | 128.22 (CH=, *J* = 13.7); 130.41 (=C<, *J* = 79.2); 131.54 (CH=, *J* = 3.2); 132.56 (CH=, *J* = 11.4) | 126.64, 127.02, 128.02, 128.67, 129.94 (CH=, *J* = 15.9); 137.05, 139.07 (=C<, *J* = 121.6) |
| **20a** | Ferrocenyl | 127.98 (CH=, *J* = 12.5); 131.03 (CH=, *J* = 3.0); 131.83 (CH=, *J* = 10.9); 133.32 (=C<, *J* = 78.5) | 69.95, 71.75 (CH=, *J* = 10.0); 73.11 (CH=, *J* = 12.6); 73.64 (=C<, *J* = 89.0) |
| **21a** | Ferrocenylene | 128.08 (CH=, *J* = 12.5); 131.19 (CH=, *J* = 3.0); 131.68 (CH=, *J* = 10.9); 132.74 (=C<, *J* = 78.6) | 74.26 (CH=, *J* = 12.0); 75.06 (=C<, *J* = 86.9); 75.21 (CH=, *J* = 9.7) |

**Selenide 17a.** White crystalline substance, m.p. 142—143 °C. Found (%): C, 68.29; H, 4.31; N, 3.15. $C_{26}H_{20}NPSe$. Calculated (%): C, 68.43; H, 4.42; N, 3.07. $^1$H NMR ($CDCl_3$), δ: 6.66 (d, 1 H, CH= of indole ring, *J* = 4.8 Hz); 7.04 (d, 1 H, CH=, Ar, *J* = 8.3 Hz); 7.14—7.34 (m, 7 H, CH=, Ar); 7.44—7.58 (m, 6 H, CH=, Ar); 7.64 (d, 1 H, CH=, Ar, *J* = 7.9 Hz); 7.86—7.96 (m, 4 H, CH=, Ar).

**Selenide 18a.** White crystalline substance, m.p. 116 °C. Found (%): C, 55.69; H, 4.27; N, 8.25. $C_{16}H_{15}N_2PSe$. Calculated (%): C, 55.66; H, 4.38; N, 8.11. $^1$H NMR ($CDCl_3$), δ: 3.83 (c, 3 H, Me); 7.14 (br.s, 1 H, —CH= of imidazole ring); 7.22 (br.s, 1 H, —CH= of imidazole ring); 7.50—7.60 (m, 6 H, —CH=, Ph); 7.82—7.90 (m, 4 H, —CH=, Ph).

**Selenide 19a.** Light pink crystalline substance, m.p. 195 °C. Found (%): C, 62.03; H, 4.34; N, 6.80. $C_{21}H_{17}N_2PSe$. Calculated (%): C, 61.92; H, 4.21; N, 6.88. $^1$H NMR ($CDCl_3$) δ,: 7.15—7.27, 7.30—7.35, 7.42—7.54, 7.86—7.94 (all m, 17 H, —CH= of imidazole ring, Ph).

**Selenide 20a.** Orange crystalline substance, decomposes at temperatures above 120 °C. Found (%): C, 58.63; H, 4.32. $C_{22}H_{19}FePSe$. Calculated (%): C, 58.83; H, 4.26. $^1$H NMR ($CDCl_3$), δ: 4.18 (s, 5 H, ferrocenyl rings); 4.47 (dd, 2 H, ferrocenyl rings, *J* = 2.1 Hz, *J* = 4.0 Hz); 4.54 (dd, 2 H, ferrocenyl rings, *J* = 1.7 Hz, *J* = 3.5 Hz); 7.40—7.50 (m, 6 H, CH=, Ph); 7.70—7.77 (m, 4 H, CH=, Ph).

**Selenide 21a.** Orange crystalline substance, decomposes at temperatures above 140 °C. Found (%): C, 57.19; H, 4.02. $C_{34}H_{28}FeP_2Se_2$. Calculated (%): C, 57.33; H, 3.96. $^1$H NMR ($CDCl_3$), δ: 4.34 (dd, 4 H, ferrocenyl rings, *J* = 1.0 Hz, *J* = 4.0 Hz); 4.73 (dd, 4 H, ferrocenyl rings, *J* = 1.0 Hz, *J* =

4.0 Hz); 7.37—7.50 (m, 12 H, CH=, Ph); 7.60—7.68 (m, 8 H, CH=, Ph).

The $^{13}C$ NMR spectra of the synthesized selenides are presented in Table 3.

## References


1. C. A. Tolman, *J. Am. Chem. Soc.*, 1970, **92**, 2956.
2. C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.
3. P. W. N. M. van Leeuwen, P. C. J. Kamer, J. N. H. Reek, and P. Dierkes, *Chem. Rev.*, 2000, **100**, 2741.
4. W. Strohmeier and F. J. Müller, *Chem. Ber.*, 1974, **96**, 53.
5. C. A. Tolman, *J. Am. Chem. Soc.*, 1970, **92**, 2953.
6. D. W. Allen and B. F. Taylor, *J. Chem. Soc.*, *Dalton Trans.*, 1982, 51.
7. C. J. Cobley and P. G. Pringle, *Inorg. Chim. Acta*, 1997, **265**, 107.
8. (a) L. Bemi, H. C. Clark, J. A. Davies, C. A. Fyfe, and R. E. Wasylishen, *J. Am. Chem. Soc.*, 1982, **104**, 438. (b) G. M. Kosolapoff and L. Maier, *Organic Phosphorus Compound*, Wiley-Interscience, New York, 1972, **1**, 106.
9. N. G. Andersen and B. A. Keay, *Chem. Rev.*, 2001, **101**, 997.
10. A. Weissberger, *Organic Solvents. Physical Properties and Methods of Purification*, Interscience Publishers, New York, 1955, 475 pp.
11. R. M. Kellogg, A. P. Schaap, E. T. Harper, and H. Wynberg, *J. Org. Chem.*, 1968, **33**, 2907.
12. Ya. L. Gol´dfarb, Yu. B. Vol´kenshtein, and B. V. Lopatin, *Zh. Obshch. Khim.*, 1964, **34**, 969 [*J. Gen. Ghem. USSR*, 1964, **34** (Engl. Transl.)].
13. A. S. Alvarez-Insua, S. Conde, and C. Corral, *J. Heterocycl. Chem.*, 1982, **19**, 713.
14. L. A. Yanovskaya and S. S. Yufit, *Organicheskii sintez v dvukhfaznykh sistemakh* [*Organic Synthesis in Two-phase Systems*], Khimiya, Moscow, 1982, p. 86 (in Russian).
15. A. F. Pozharskii, B. K. Martsokha, and A. M. Simonov, *Zh. Obshch. Khim.*, 1963, **33**, 1005 [*J. Gen. Chem. USSR*, 1963, **33** (Engl. Transl.)].
16. W. E. McEwen, J. E. Fountaine, D. N. Schulz, and W.-I. Shiau, *J. Org. Chem.*, 1976, **41**, 1684.
17. H. Schindlbauer, *Chem. Ber.*, 1967, **100**, 3432.
18. S. O. Grim, W. McFarlane, and E. F. Davidoff, *J. Org. Chem.*, 1967, **32**, 781.
19. K. Issleib and H. Völker, *Chem. Ber.*, 1961, **94**, 392.
20. K. A. Petrov, E. E. Nifant´ev, T. N. Lysenko, and V. P. Evdakov, *Zh. Obshch. Khim.*, 1961, **31**, 2377 [*J. Gen. Chem. USSR*, 1961, **31** (Engl. Transl.)].
21. G. P. Sollott, H. F. Mertwoy, S. Portnoy, and J. L. Snead, *J. Org. Chem.*, 1963, **28**, 1090.
22. J. J. Bishop, A. Davison, M. L. Katcher, D. W. Lichtenberg, R. E. Merrill, and J. C. Smart, *J. Organomet. Chem.*, 1971, **27**, 241.


*Received January 21, 2002;*
*in revised form July 12, 2002*