# [4+2] Cycloaddition reactions of 1-alkyl-2,3,4,5-tetraphenylphosphole derivatives*

*A. A. Zagidullin,★ E. S. Grigoreva, A. V. Petrov, R. P. Shekurov, and V. A. Milyukov*

*Arbuzov Institute of Organic and Physical Chemistry,*
*Federal Research Center "Kazan Scientific Center of the Russian Academy of Sciences,"*
*8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation.*
*E-mail: zagidullin@iopc.ru*

The [4+2] cycloaddition reactions of 1-alkyl-2,3,4,5-tetraphenylphosphole derivatives with *N*-phenylmaleimide were studied for the first time. The reactions of 1-alkyl-2,3,4,5-tetraphenylphosphole oxides and sulfides with *N*-phenylmaleimide leads to tricyclic 10-phosphanorbornenes with high stereoselectivity, giving only one diastereomer in the racemic form. At the same time, 1-alkyl-2,3,4,5-tetraphenylphospholes and their $W(CO)_5L$ complexes do not undergo [4+2] cycloaddition reactions even upon prolonged heating.

**Key words:** phosphorus heterocycles, monophosphole, cycloaddition reactions, phosphanorbornene.

Phosphacyclopentadienes (phospholes),[1] phosphorus analogs of cyclopentadiene, attract close attention, since they are convenient synthons for the preparation of polycyclic phosphorus-containing compounds,[2] phosphacyclopentadienide anions and phosphametallocenes,[3] phosphabenzenes.[4,5] Cycloaddition reactions of phosphacyclopentadienes have been successfully used for the synthesis of new chiral polycyclic phosphorus compounds such as phosphanorbornenes and phosphanorbornadienes, which have found application as ligands for transition metal complexes[6—9] and organocatalysts[10] for asymmetric catalysis. Besides, the cycloaddition reactions of phospholes to substituted acetylenes are a convenient method for the generation of phosphorus analogs of carbenes, phosphinidenes,[11—13] and the synthesis of phosphabenzenes, the phosphorus analogs of pyridine, which are a promising class of phosphorus ligands for homogeneous catalysis.[14—16]

At present, out of all phospholes the chemical behavior of monophosphacyclopentadienes is most fully studied, which allowed one to reveal significant differences in the reactivity and stability of two tautomeric forms, namely, 1*H*- and 2*H*-phospholes. While 1*H*-phospholes possess high thermal stability and undergo cycloaddition reactions only under extremely harsh conditions, giving low yields of the target products, 2*H*-phospholes formed from 1*H*-phospholes by the *R*-[1,5]-sigmatropic shift at high temperatures, contain a highly reactive P=C bond and readily undergo cycloaddition reactions with both dienes and dienophiles.[17,18] Several methods have been described to increase the reactivity of phospholes in cycloaddition reactions.[1] One of them is the replacement of the carbon atom in the exocyclic P—C bond of monophospholes with a more electronegative heteroatom (N, O)[19,20] or the introduction of electronegative substituents in the heterocycle,[21] which reduces the effect of hyperconjugation with the double bond and activates phospholes in cycloaddition reactions. Another method is to block a lone electron pair (LEP) of the phosphorus atom by coordination with a metal,[1,22] sulfur,[23] or oxygen atoms.[24—26]

Earlier, we have developed a new method for the synthesis of 1-alkyl-2,3,4,5-tetraphenylphospholes based on the alkylation of alkali metal 2,3,4,5-tetraphenylmonophospholides obtained by the reaction of white phosphorus or sodium polyphospholides with 1,4-dilithiumbuta-1,3-diene[27] or diphenylacetylene,[28] respectively. In this connection, it was of interest to study [4+2] cycloaddition reactions of 1-alkyl-2,3,4,5-tetraphenylphospholes and their derivatives (oxides, sulfides, and metal complexes) in order to obtain new polycyclic phosphorus compounds.

## Results and Discussion

The starting 1-alkyl-2,3,4,5-tetraphenylphospholes **1**, their oxides and sulfides were obtained according to the described procedures.[27,28] To obtain complexes of monophospholes **1** with $W(CO)_6$, we used a technique of "indirect" photochemical substitution of the carbonyl group, which is based on UV irradiation of a solution of tungsten hexacarbonyl in THF with the formation of a labile complex $W(CO)_5THF$ existing only in solution. The addition

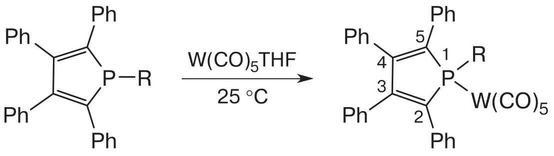
---

* Based on the materials of the International Markovnikov Congress on Organic Chemistry (June 21—28, 2019, Moscow—Kazan, Russia).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 0492—0495, March, 2020.

to the latter of the corresponding ligands **1a** and **1b** allows one to replace the THF molecule without irradiation and to obtain monosubstituted tungsten carbonyl complexes **2a** and **2b** containing monophospholes **1** and isolated as red powders in 89—92% yield (Scheme 1).

**Scheme 1**



**1a,b** **2a,b**

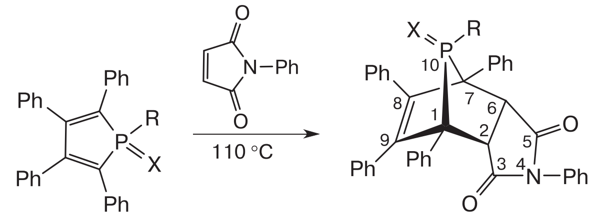
R = $Pr^i$ (**a**), $n$-$C_8H_{17}$ (**b**)

The structures of complexes **2** were determined by IR, $^1H$, $^{31}P$, and $^{13}C$ NMR spectroscopy, their composition was confirmed by elemental analysis. Thus, the $^{31}P\{1H\}$ NMR spectrum of complex **2a** exhibits a singlet at $\delta_P$ 45.4 with the spin-spin coupling constant $^1J_{W,P}$ = 215.9 Hz. The $^1H$ and $^{13}C$ NMR spectra unambiguously confirm the structure of complex **2a**. The IR spectrum of (1-isopropyl-2,3,4,5-tetraphenylphosphole)tungsten pentacarbonyl (**2a**) contains four absorption bands (KBr), ν(CO)/$cm^{-1}$: 1937, 2019, 2070, 2128 characteristic of complexes with the formula $W(CO)_5L$.

The reactivity of 2,3,4,5-tetraphenylphospholes **1** and their derivatives **2—4** was investigated using the [4+2] cycloaddition reaction to *N*-phenylmaleimide as an example. We found that 2,3,4,5-tetraphenylphospholes **1** and their tungsten complexes **2** do not undergo the [4+2] cycloaddition to *N*-phenylmaleimide even upon prolonged heating at 170 °C for 20 h, probably, due to the σ—π-hyperconjugation between the molecular orbital of the P—R fragment and the diene system.[29] Note that 2,3,4,5-tetraphenylphospholes **1** do not undergo *R*-[1,5]-sigmatropic shift to form highly reactive 2*H*-phospholes with the P=C double bond, as is observed in the case of 3,4-dimethyl-1-phenylphosphole.[17]

At the same time, 1-alkyl-2,3,4,5-tetraphenylphosphole 1-oxides **3** and 1-alkyl-2,3,4,5-tetraphenylphosphole 1-sulfides **4** undergo cycloaddition reactions to *N*-phenylmaleimide. It was found that the products of [4+2] cycloaddition reaction are formed upon heating of compounds **3** and **4** with *N*-phenylmaleimide at 110 °C for 2 days in high yields (81—87%) (Scheme 2).

**Scheme 2**



**3a,b**, **4a,b** **5a,b**, **6a,b**

X = O (**3**, **5**), S (**4**, **6**)
R = $Pr^i$ (**a**), $n$-$C_8H_{17}$ (**b**)

The structures of cycloadducts **5** and **6** were determined by IR, $^1H$, $^{31}P$, and $^{13}C$ NMR spectroscopy, their composition was confirmed by mass-spectrometry and elemental analysis. Thus, the $^{31}P$ NMR spectra of reaction mixtures and isolated products exhibit a singlet at $\delta_P$ 97 for phosphanorbornene oxides **5a,b** and a singlet at $\delta_P$ 116 for phosphanorbornene sulfides **6a,b**, which indicates a high selectivity of this reaction. Analysis of the $^1H$ NMR spectra confirmed the formation of only one diastereoisomer in racemic form: only one group of signals is observed in the range of δ 4.25—4.38, namely, a doublet with $^3J_{P,H} \approx 7.5$ Hz for the protons of the *N*-phenylmaleimide fragment of products **5** and **6**. The $^{13}C$ NMR spectra exhibit a singlet at δ 62 for carbon atoms C(2) and C(6) of the *N*-phenylmaleimide fragment and a doublet at δ 73 with $^1J_{C,P} \approx 34$ Hz for carbon atoms C(1) and C(7) of the phosphanorbornene fragment of the [4+2] cycloaddition products. Although we did not succeed in obtaining crystals suitable for X-ray diffraction, we presume the formation of *anti*-, *endo*-isomers, as occurs in the case of structurally similar 1-alkyl-3,4,5-triphenyl-1,2-diphospholes.[30,31] We note that in the case of oxides and sulfides of 2,3,4,5-tetraphenylphospholes **3** and **4**, no formation of *endo*-dimers occurs by the [4+2] cycloaddition reaction between two phosphole molecules, as is observed in the case of 1-alkyl-3-methylphospholes.[24,25]

In conclusion, we have shown that 1-alkyl-2,3,4,5-tetraphenylphospholes **1**, as well as their complexes $W(CO)_5L$ **2**, do not undergo the [4+2] cycloaddition reaction to *N*-phenylmaleimide. At the same time, the oxidation and thiooxidation of the phosphorus atom in 1-alkyl-2,3,4,5-tetraphenylphospholes **1** increases their reactivity, leading to the formation of [4+2] cycloaddition products with *N*-phenylmaleimide upon prolonged heating at 110 °C, which are tricyclic 10-phosphanorbornenes **5** and **6**. This occurs due to the blockage of the LEP of the phosphorus atom by the oxygen or sulfur atom, which leads to a decrease in the aromaticity of monophosphole ("aromaticity — antiaromaticity" transition[32]) and an increase in its reactivity.

## Experimental

All the works related to the preparation of starting reagents, synthesis, and isolation of products were carried out under an inert atmosphere using standard Schlenk equipment. All the solvents were distilled over Na/benzophenone or $P_2O_5$ immediately before use. NMR spectra were recorded on a Bruker MSL-

400 spectrometer ($^1$H 400 MHz, $^{31}$P 121.7 MHz, $^{13}$C 100.6 MHz) using $SiMe_4$ as an internal standard for $^1$H and $^{13}$C NMR spectra and 85% $H_3PO_4$ as an external standard for $^{31}$P NMR spectra. The spectra were recorded for 10—20% solutions in inert solvents ($CDCl_3$). Elemental analysis was performed using an EuroVector EA 3000 CHNS-O automated analyzer. 1-Alkyl-2,3,4,5-tetraphenylphospholes **1a,b**, their oxides **3a,b** and sulfides **4a,b** were obtained according to the described procedures.[27,28] Tungsten hexacarbonyl and *N*-phenylmaleimide are commercially available reagents and were used without additional purification.

**Synthesis of (1-isopropyl-2,3,4,5-tetraphenylphosphole)tungsten pentacarbonyl (2a) (general procedure).** A solution of 0.35 g (1 mmol) of tungsten hexacarbonyl in tetrahydrofuran (100 mL) was irradiated with UV light in a quartz reactor for 3 h at 5 °C under continuous flow of argon. A solution of 1-isopropyl-2,3,4,5-tetraphenylphosphole (**1a**) (0.42 g, 1 mmol) in tetrahydrofuran (10 mL) was added to the resulting lemon-yellow solution and the mixture was stirred for 12 h. The solvent was evaporated *in vacuo*, the residue was extracted with *n*-hexane (40 mL) and filtered. The hexane extract was concentrated under reduced pressure, the residue was dried *in vacuo* to obtain **2a** as a red powder The yield was 0.67 g (89%), m.p. 134 °C. $^{31}$P NMR ($CDCl_3$), δ: 45.4 (s, $^1J_{P,W}$ = 215.9 Hz). $^1$H NMR ($CDCl_3$), δ: 1.26 (dd, 6 H, $CH_3$, $^3J_{P,H}$ = 7.2 Hz, $^3J_{H,H}$ = 15.9 Hz); 2.71—2.81 (m, 1 H, CH); 6.81—7.57 (m, 2 H, Ph); 7.01—7.32 (m, 14 H, Ph); 7.46—7.65 (m, 2 H, Ph); 7.80—7.87 (m, 2 H, Ph). $^{13}$C NMR ($CDCl_3$), δ: 20.2 (s, $CH_3$); 28.2 (d, CH, $^1J_{C,P}$ = 23.1 Hz); 126.7 (s, *p*-$C_{Ph}$); 127.4 (s, *p*-$C_{Ph}$); 127.9 (s, *m*-$C_{Ph}$); 128.3 (s, *m*-$C_{Ph}$); 129.6 (s, *o*-$C_{Ph}$); 130.5 (s, *o*-$C_{Ph}$); 131.6 (s, *ipso*-$C_{Ph}$); 137.9 (s, *ipso*-$C_{Ph}$); 145.1 (s, C(3)/C(4)); 151.4 (d, C(2)/C(5), $^1J_{C,P}$ = 17.2 Hz). IR (KBr), ν(CO)/cm$^{-1}$: 1937, 2019, 2070, 2128. Found (%): C, 57.64; H, 3.93; P, 4.17. $C_{36}H_{27}O_5PW$ (M 619). Calculated (%): C, 57.31; H, 3.61; O, 10.60; P, 4.11; W, 24.37.

**(1-*n*-Octyl-2,3,4,5-tetraphenylphosphole)tungsten pentacarbonyl (2b).** A similar reaction of tungsten hexacarbonyl (0.35 g, 1 mmol) and 1-*n*-octyl-2,3,4,5-tetraphenylphosphole **1b** (0.50 g, 1 mmol) gave compound **2b** (0.75 g, 92%) as a red powder with m.p. 142 °C. $^{31}$P NMR ($CDCl_3$), δ: 40.2 (s, $^1J_{P,W}$ = 223.1 Hz). $^1$H NMR ($CDCl_3$), δ: 0.87 (t, 3 H, $CH_3$, $^3J_{H,H}$ = 7.0 Hz); 1.13—1.43 (m, 12 H, $(CH_2)_6$); 2.14—2.18 (m, 2 H, P—$CH_2$); 6.98—7.37 (m, 2 H, Ph); 7.01—7.32 (m, 14 H, Ph); 7.46—7.70 (m, 4 H, Ph). $^{13}$C NMR ($CDCl_3$), δ: 14.2 (s, $CH_3$); 22.4, 24.7, 28.5, 28.9, 29.2, 30.1 (s, $CH_2$); 34.8 (d, P—$CH_2$, $^1J_{P,C}$ = 20.1 Hz); 126.7 (s, *p*-$C_{Ph}$); 127.4 (s, *p*-$C_{Ph}$); 127.5 (s, *m*-$C_{Ph}$); 128.6 (s, *m*-$C_{Ph}$); 129.1 (s, *o*-$C_{Ph}$); 130.5 (s, *o*-$C_{Ph}$); 131.6 (s, *ipso*-$C_{Ph}$); 134.4 (s, *ipso*-$C_{Ph}$); 145.2 (d, C(3)/C(4), $^2J_{C,P}$ = 6.6 Hz); 152.9 (d, C(2)/C(5), $^1J_{C,P}$ = 17.5 Hz). IR (KBr), ν(CO)/cm$^{-1}$: 1933, 2048, 2072, 2136. Found (%): C, 60.01; H, 4.33; P, 3.85. $C_{41}H_{37}O_5PW$ (M 824). Calculated (%): C, 59.72; H, 4.52; O, 9.70; P, 3.76; W, 22.30.

**Synthesis of 10-isopropyl-10-oxo-1,4,7,8,9-pentaphenyl-4-aza-10-phosphatricyclo[5.2.1.0$^{2,6}$]dec-8-en-3,5-dione (5a) (general procedure).** *N*-phenylmaleimide (0.077 g, 0.45 mmol) was added to compound **3a** (0.20 g, 0.45 mmol) and the mixture was heated in toluene at 110 °C for 50 h. After two days, a light yellow precipitate was formed, which was collected by filtration and dried *in vacuo*. Recrystallization from hot toluene (5 mL), filtration, and vacuum drying of the precipitate gave **5a** as a light yellow powder (0.24 g, 86%), m.p. 175 °C. $^{31}$P NMR ($CDCl_3$), δ: 98.7 (s). $^1$H NMR ($CDCl_3$), δ: 1.26 (dd, 6 H, $CH_3$, $^3J_{H,H}$ = = 13.8 Hz, $^3J_{P,H}$ = 6.9 Hz); 2.83—2.88 (m, 1 H, CH); 4.33 (d, 2 H, C(2)—H/C(6)—H, $^3J_{P,H}$ = 7.4 Hz); 7.05—7.22 (m, 5 H, Ph); 7.35—7.43 (m, 12 H, Ph); 7.46—7.55 (m, 8 H, Ph). $^{13}$C NMR ($CDCl_3$), δ: 16.3 (d, $CH_3$, $^2J_{C,P}$ = 6.9 Hz); 28.0 (d, CH, $^1J_{C,P}$ = 31.8 Hz); 63.2 (s, C(2)/C(6)); 75.1 (d, C(1)/C(7)); 126.1 (s, *p*-$C_{Ph}$); 126.4 (s, *p*-$C_{Ph}$); 127.4 (s, *p*-$C_{Ph}$); 127.6 (s, *m*-$C_{Ph}$); 127.8 (s, *m*-$C_{Ph}$); 128.3 (s, *m*-$C_{Ph}$); 129.1 (s, *o*-$C_{Ph}$); 129.2 (s, *o*-$C_{Ph}$); 130.5 (s, *o*-$C_{Ph}$); 130.8 (s, *ipso*-$C_{Ph}$); 134.1 (s, *ipso*-$C_{Ph}$); 137.5 (d, *ipso*-$C_{Ph}$, $^2J_{C,P}$ = 7.5 Hz); 148.2 (d, C(8)=C(9), $^2J_{C,P}$ = 6.9 Hz); 175.7 (d, C(3)/C(5), $^3J_{C,P}$ = 2.9 Hz). IR (KBr), ν/cm$^{-1}$: 1262 (m, P=O); 1768 (s, CO). Found (%): C, 79.64; H, 5.93; N, 2.42; P, 5.54. $C_{41}H_{34}NO_3P$ (M 619). Calculated (%) C, 79.47; H, 5.53; N, 2.26; P, 5.00.

**10-*n*-Octyl-10-oxo-1,4,7,8,9-pentaphenyl-4-aza-10-phosphatricyclo[5.2.1.0$^{2,6}$]dec-8-en-3,5-dione (5b).** A similar reaction of compound **4b** (0.41 g, 0.79 mmol) and *N*-phenylmaleimide (0.14 g, 0.79 mmol) gave compound **5b** (0.44 g, 81%) as a light yellow powder with m.p. 181 °C. $^{31}$P NMR ($CDCl_3$), δ: 96.7 (s). $^1$H NMR ($CDCl_3$), δ: 1.07 (t, 3 H, $CH_3$, $^3J_{H,H}$ = 8.0 Hz); 1.18—1.49 (m, 12 H, $(CH_2)_6$); 2.04—2.15 (m, 2 H, P—$CH_2$); 4.25 (d, 2 H, C(2)—H/C(6)—H, $^3J_{P,H}$ = 7.5 Hz); 7.03—7.21 (m, 5 H, Ph); 7.33—7.51 (m, 20 H, Ph). $^{13}$C NMR ($CDCl_3$), δ: 14.6 (s, $CH_3$); 22.4, 24.6, 28.5, 28.7, 29.4, 30.2 (s, $CH_2$); 29.8 (d, P—$CH_2$, $^1J_{P,C}$ = 38.2 Hz), 62.6 (s, C(2)/C(6)); 71.7 (d, C(1)/C(7), $^1J_{C,P}$ = 34.8 Hz); 126.8 (s, *p*-$C_{Ph}$); 126.9 (s, *p*-$C_{Ph}$); 127.4 (s, *p*-$C_{Ph}$); 127.8 (s, *m*-$C_{Ph}$); 128.1 (s, *m*-$C_{Ph}$); 128.7 (s, *m*-$C_{Ph}$); 129.0 (s, *o*-$C_{Ph}$); 129.2 (s, *o*-$C_{Ph}$); 130.3 (s, *o*-$C_{Ph}$); 130.8 (s, *ipso*-$C_{Ph}$); 134.8 (s, *ipso*-$C_{Ph}$); 137.1 (d, *ipso*-$C_{Ph}$,$^2J_{C,P}$ = 7.6 Hz); 147.2 (d, C(8)=C(9), $^2J_{C,P}$ = 6.9 Hz); 172.9 (d, C(3)/C(5), $^3J_{CP}$ = 2.9 Hz). IR (KBr), ν/cm$^{-1}$: 1258 (s, P=O), 1770 (m, CO). Found (%): C, 79.84; H, 6.33; N, 2.12; P, 4.84. $C_{46}H_{44}NO_3P$ (M 689). Calculated (%): C, 80.09; H, 6.43; N, 2.03; P, 4.49.

**10-Isopropyl-1,4,7,8,9-pentaphenyl-10-thioxo-4-aza-10-phosphatricyclo[5.2.1.0$^{2,6}$]dec-8-en-3,5-dione (6a).** A similar reaction of compound **4a** (0.29 g, 0.62 mmol) and *N*-phenylmaleimide (0.11 g, 0.62 mmol) gave **6a** (0.35 g, 87%) as a light yellow powder with m.p. 176—177 °C. $^{31}$P NMR ($CDCl_3$), δ: 118.3 (s). $^1$H NMR ($CDCl_3$), δ: 1.23 (dd, 6 H, $CH_3$, $^3J_{H,H}$ = = 13.7 Hz, $^3J_{P,H}$ = 6.9 Hz); 2.74—2.81 (m, 1 H, CH); 4.36 (d, 2 H, C(2)—H/C(6)—H, $^3J_{P,H}$ = 7.4 Hz); 7.09—7.22 (m, 5 H, Ph); 7.35—7.55 (m, 20 H, Ph). $^{13}$C NMR ($CDCl_3$), δ: 16.9 (d, $CH_3$, $^2J_{C,P}$ = 6.6 Hz); 29.6 (d, CH, $^1J_{C,P}$ = 31.8 Hz); 61.2 (s, C(2)/C(6)); 74.8 (d, C(1)/C(7)); 126.1 (s, *p*-$C_{Ph}$); 127.1 (s, *p*-$C_{Ph}$); 127.7 (s, *p*-$C_{Ph}$); 127.9 (s, *m*-$C_{Ph}$); 128.3 (s, *m*-$C_{Ph}$); 128.7 (s, *m*-$C_{Ph}$); 129.3 (s, *o*-$C_{Ph}$); 129.7 (s, *o*-$C_{Ph}$); 131.5 (s, *o*-$C_{Ph}$); 132.8 (s, *ipso*-$C_{Ph}$); 134.1 (s, *ipso*-$C_{Ph}$); 136.3 (d, *ipso*-$C_{Ph}$, $^2J_{C,P}$ = 7.3 Hz); 146.9 (d, C(8)=C(9), $^2J_{C,P}$ = 7.1 Hz); 174.1 (d, C(3)/C(5), $^3J_{C,P}$ = 3.2 Hz). IR (KBr), ν/cm$^{-1}$: 1774 (s, CO). Found (%): C, 77.64; H, 5.12; N, 2.17; P, 5.41. $C_{41}H_{34}NO_2PS$ (M 635). Calculated (%): C, 77.46; H, 5.39; N, 2.20; P, 5.03.

**10-*n*-Octyl-1,4,7,8,9-pentaphenyl-10-thioxo-4-aza-10-phosphatricyclo[5.2.1.0$^{2,6}$]dec-8-en-3,5-dione (6b).** A similar reaction of compound **4b** (0.28 g, 0.53 mmol) and *N*-phenylmaleimide (0.09 g, 0.53 mmol) gave **6b** (0.31 g, 83%) as a light yellow powder with m.p. 179—180 °C. $^{31}$P NMR ($CDCl_3$), δ: 115.6 (s). $^1$H NMR ($CDCl_3$), δ: 0.97 (t, 3 H, $CH_3$, $^3J_{H,H}$ = 7.1 Hz); 1.25—1.62 (m, 12 H, $(CH_2)_6$); 1.98—2.03 (m, 2 H, P—$CH_2$); 4.38 (d, 2 H, C(2)—H/C(6)—H, $^3J_{P,H}$ = 6.5 Hz); 7.07—7.22

(m, 5 H, Ph); 7.33—7.42 (m, 12 H, Ph); 7.48—7.55 (m, 8 H, Ph). $^{13}$C NMR (CDCl$_3$), δ: 15.5 (s, CH$_3$); 20.4, 22.3, 25.5, 26.7, 28.4, 30.2 (s, CH$_2$); 31.1 (d, P—CH$_2$, $^1J_{\mathrm{P,C}}$ = 36.2 Hz); 62.7 (s, C(2)/C(6)); 72.7 (d, C(1)/C(7) , $^1J_{\mathrm{C,P}}$ = 31.2 Hz); 126.5 (s, *p*-C$_{\mathrm{Ph}}$); 126.9 (s, *p*-C$_{\mathrm{Ph}}$); 127.4 (s, *p*-C$_{\mathrm{Ph}}$); 127.9 (s, *m*-C$_{\mathrm{Ph}}$); 128.3 (s, *m*-C$_{\mathrm{Ph}}$); 128.6 (s, *m*-C$_{\mathrm{Ph}}$); 129.0 (s, *o*-C$_{\mathrm{Ph}}$); 129.2 (s, *o*-C$_{\mathrm{Ph}}$); 130.2 (s, *o*-C$_{\mathrm{Ph}}$); 131.0 (s, *ipso*-C$_{\mathrm{Ph}}$); 134.2 (s, *ipso*-C$_{\mathrm{Ph}}$); 137.7 (d, *ipso*-C$_{\mathrm{Ph}}$, $^2J_{\mathrm{C,P}}$ = 7.6 Hz); 147.8 (d, C(8)=C(9)), 173.3 (d, C(3)/C(5), $^3J_{\mathrm{C,P}}$ = 2.9 Hz). IR (KBr), ν/cm$^{-1}$: 1778 (m, CO). Found (%): C, 78.24; H, 6.33; N, 2.05; P, 4.74. $C_{46}H_{44}NO_2PS$ (M 706). Calculated (%): C, 78.27; H, 6.28; N, 1.98; P, 4.39.

This work was financially supported by the Russian Foundation for Basic Research and the Government of the Republic of Tatarstan in the framework of the scientific Project No. 18-43-160025.

The authors gratefully acknowledge the Assigned Spectral-Analytical Center for Study of Structure, Composition and Properties of Substances and Materials of FRC "Kazan Scientific Center of the Russian Academy of Sciences" for technical support of the research.

## References

1. A. A. Zagidullin, I. A. Bezkishko, V. A. Miluykov, O. G. Sinyashin, *Mendeleev. Commun.*, 2013, **23**, 117.
2. F. Mathey, *Acc. Chem. Res.*, 2004, **37**, 954.
3. I. A. Bezkishko, A. A. Zagidullin, V. A. Miluykov, O. G. Sinyashin, *Russ. Chem. Rev.*, 2014, **83)**, 555.
4. J. Grundy, F. Mathey, *Angew. Chem., Int. Ed.*, 2005, **44**, 1082.
5. H. Wang, C. Li, D. Geng, H.Chen, Z. Duan, F. Mathey, *Chem. Eur. J.*, 2010, **16**, 10659.
6. M. Zhi, Z. Gan, R. Ma, H. Cui, E.-Q. Li, Z. Duan, F. Mathey, *Org. Lett.*, 2019, **21**, 3210.
7. Z. Gan, M. Zhi, R. Han, E.-Q. Li, Z. Duan, F. Mathey, *Org. Lett.*, 2019, **21**, 2782.
8. F. Mercier, F. Brebion, R. Dupont, F. Mathey, *Tetrahedron: Asymmetry*, 2003, **14**, 3137.
9. A. A. Zagidullin, E. S. Oshchepkova, I. V. Chuchelkin, S. A. Kondrashova, V. A. Miluykov, Sh. K. Latypov, K. N. Gavrilov, E. Hey-Hawkins, *Dalton Trans.*, 2019, **48**, 4677.
10. A. A. Zagidullin, V. A. Miluykov, O. G. Sinyashin, E. Hey-Hawkins, *Catal Today.*, 2017, **279**, 142.
11. A. Marinetti, F. Mathey, J. Fischer, A. Mitschler, *J. Am. Chem. Soc.*, 1982, **104**, 4484.
12. K. Lammertsma, A. Ehlers, M. McKee, *J. Am. Chem. Soc.*, 2003, **125**, 14750.
13. V. A. Miluykov, A. A. Zagidullin, O. G. Sinyashin, E. Hey-Hawkins, *Russ. J. Coord. Chem.*, 2010, **36**, 891.
14. J. Leitl, M. Marquardt, P. Coburger, D. J. Scott, V. Streitferdt, R. M. Gschwind, C. Müller, R. Wolf, *Angew. Chem.*, *Int. Ed.*, 2019, **58 (43)**, 15407.
15. A. Loibl, I. Krom, E. Pidko, M. Weber, J. Wiecko, C. Müller, *Chem. Commun.*, 2014, **50**, 8842.
16. A. A. Zagidullin, Y. S. Ganushevich, A. G. Kafiyatullina, V. A. Miluykov, O. G. Sinyashin, *Russ. Chem. Bull.*, 2015, **64**, 1986.
17. C. Charrier, H. Bonnard, G. Lauzon, F. Mathey, *J. Am. Chem. Soc.*, 1983, **105**, 6871.
18. L. D. Quin, *Curr. Org. Chem.*, 2006, **10**, 43.
19. E. Mattmann, D. Simonutti, L. Ricard, F. Mercier, F. Mathey, *J. Org. Chem.*, 2001, **66**, 755.
20. E. Mattmann, F. Mercier, L. Ricard, F. Mathey, *J. Org. Chem.*, 2002, **67**, 5422.
21. A. Zagidullin, V. Miluykov, E. Oschepkova, A. Tufatullin, O. Kataeva, O. Sinyashin, *Beilstein J. Org. Chem.*, 2015, **11**, 169.
22. J. Svara, A. Marinetti, F. Mathey, *Organometallics*, 1986, **5**, 1161.
23. S. Holand, F. Mathey, *J. Org. Chem.*, 1981, **46**, 4386.
24. T. Kovács, L. S. Fülöp, Z. Mucsi, K. Karaghiosoff, M. Czugler, G. Keglevich, *Heteroat. Chem.*, 2015, **26**, 335.
25. J. Kovács, N. B. Szabó, Z. Nagy, K. Ludányi, G. Keglevich, *Heteroat. Chem.*, 2005, **16**, 320.
26. A. Zagidullin, Y. Ganushevich, V. Miluykov, D. Krivolapov, O. Kataeva, O. Sinyashin, E. Hey-Hawkins, *Org. Biomol. Chem.*, 2012, **10**, 5298.
27. E. Oshchepkova, A. Zagidullin, T. Burganov, S. Katsyuba, V. Miluykov, O. Lodochnikova, *Dalton Trans.*, 2018, **47**, 11521.
28. A. V. Petrov, A. A. Zagidullin, T. I. Burganov, N. I. Shatalova, S. A. Katsyuba, V. A. Milyukov, *Russ. Chem. Bull.*, 2019, **68**, 445.
29. L. Nyul´aszi, *Chem. Rev.*, 2001, **101**, 1229.
30. A. Zagidullin, Y. Ganushevich, V. Miluykov, O. Sinyashin, E. Hey-Hawkins, *Phosphorus, Sulfur, Silicon Relat. Elem.*, 2013, **188**, 238.
31. A. Zagidullin, V. Miluykov, O. Sinyashin, P. Lonnecke, E. Hey-Hawkins, *Heteroat. Chem.*, 2014, **25**, 28.
32. L. Nyulaszi, O. Holloczki, C. Lescop, M. Hissler, R. Reau, *Org. Biomol. Chem.*, 2006, **4**, 996.

*Received December 2, 2019;*
*in revised form January 13, 2020;*
*accepted January 14, 2020*