Trisodium heptaphosphide in reactions with alkyl and aryl tosylates

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Reactions of trisodium heptaphosphide with alkyl tosylates gave dialkylheptaphosphides or trialkylheptaphosphines, depending on the stoichiometric ratios of the starting reagents. A method for determination of the coupling constants of the asymmetric isomer of trialkylheptaphosphines was proposed. Reactions of the heptaphosphide trianion with aryl tosylates yielded disodium hexadecaphosphide.

Key words: trisodium heptaphosphide, alkyl tosylates, aryl tosylates, alkylheptaphosphines, disodium hexadecaphosphide.

Development of new methods for the synthesis of practically useful organophosphorus derivatives directly from white phosphorus is a topical problem in organophosphorus chemistry.[1] At the same time, the chemical properties of alkali metal polyphosphides, which are intermediates in the transformations of the elemental phosphorus molecule (in particular, the most accessible heptaphosphide trianion), have not been studied extensively in reactions with organic substrates.[2,3] It has been demonstrated[4—6] that trilithium heptaphosphide reacts with alkyl halides to give a mixture of di- and trialkylheptaphosphines. Reactions of tetraalkylammonium salts with the heptaphosphide trianion yield the asymmetric isomers of dialkylheptaphosphide only.[7]

Our attention has been attracted by the known reaction of alkali metal phosphides with alkyl and aryl tosylates, which occurs under mild conditions to give the desired tertiary phosphines in good yields (Scheme 1).[8]

Scheme 1

$$R_2PNa + R{-}O{-}Ts \longrightarrow R_2P{-}R + NaO{-}Ts$$

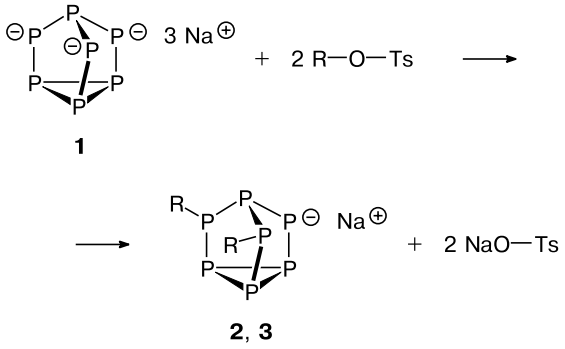
Although this reaction works well in the alkylation of simplest phosphides, the possibility of applying it to polyphosphide systems has not been investigated to date.

The goal of the present work was to study reactions of trisodium heptaphosphide (**1**) with alkyl tosylates, determine the factors that affect the yields and structures of the reaction products, and examine their structures by ^{31}P NMR spectroscopy.

Results and Discussion

We found that reactions of heptaphosphide **1** with alkyl tosylates (2 equiv.) give dialkylheptaphosphides **2** and **3** as the major products (Scheme 2).

Scheme 2



R = Pr^i (**2**), Bu^i (**3**)

The ^{31}P NMR spectrum of the reaction mixture shows five groups of signals at δ 52, −46, −124, −129, and −163, which indicates the formation of only one asymmetric isomer of sodium dialkylheptaphosphide. The signal at

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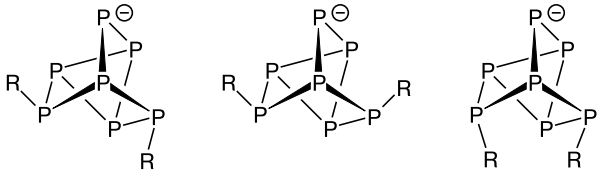
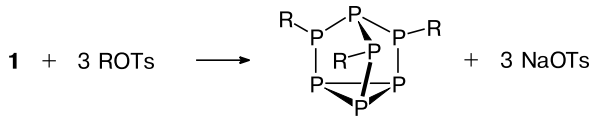
δ 52 due to two alkylated P atoms appears as a doublet of doublets, which matches the isomer *asym*-1. In the case of the isomer *asym*-2, this signal is transformed into a pseudotriplet.[9]



sym *asym*-1 *asym*-2

At the same time, the reactions of heptaphosphide **1** with three or more equivalents of alkyl tosylates gave trialkylheptaphosphines **4**—**8** only; their structures were proven by ^1H and ^{31}P NMR spectroscopy and their compositions were confirmed by elemental analysis (Scheme 3).

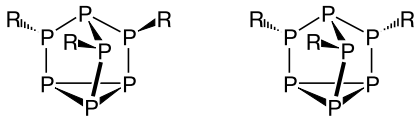
Scheme 3



4—**8**

R = Bu (**4**), C_6H_{13} (**5**), Bu^i (**6**), Pr^i (**7**), 3-C_5H_{11} (**8**)

The ^{31}P NMR spectra of trialkylheptaphosphines **4**—**8** contain ten groups of signals, which is indicative of the presence of a mixture of the symmetric and asymmetric isomers in solution. This is associated with different orientations of the alkyl groups relative to each other.



s *a*

sym *asym*

The ^{31}P NMR spectra of the asymmetric isomers of compounds **4**—**8** (*a*-**4**—*a*-**8**) consist of seven groups of signals corresponding to the ABCMXYZ spin system of first-order spectra ($\Delta\upsilon \gg J$). Each group contains $2^6 = 64$ spectral lines due to couplings with the other six P atoms. A detailed analysis of each group allowed us to calculate 21 spin-spin coupling constants, which fully characterize this system. The experimental and simulated spectra (calculated from the constants obtained by the SPINWORKS[10] and PERCH programs[11]) of the asymmetric isomer of tris(3-pentyl)heptaphosphine (*a*-**8**) are shown in Fig. 1. Their virtually complete identity suggests the correctness of the proposed method for determination of the coupling constants for the asymmetric isomers of trialkylheptaphosphines **4**—**8**.

The ^{31}P NMR spectra of the symmetric isomers of trialkylheptaphosphines *s*-**4**—*s*-**8** contain only three groups of signals: at δ 90 (alkylated P(2) atoms), −112 (apical P(1) atom), and −165 (basal P(3) atoms); this provides evidence for the equivalence of both the alkylated and basal phosphorus atoms in the P_7 framework. Thus, the spectrum of the symmetric isomer is a degenerate case of

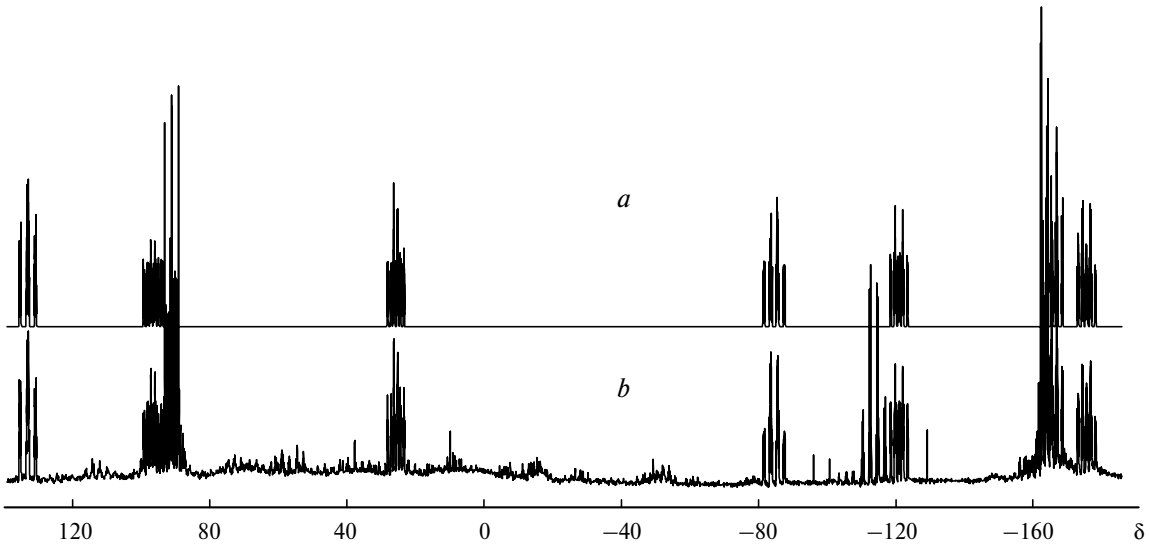


Fig. 1. ^{31}P NMR spectra of tris(3-pentyl)heptaphosphine (**8**): calculated for the asymmetric isomer (*a*) and experimental (*b*) (spin system ABCMXYZ).

the spectrum of the asymmetric isomer, is characterized by the AA′A″MXX′X″ spin system, and is a higher-order spectrum.

An analysis of the ^{31}P NMR spectra of trialkylheptaphosphines **4**—**8** revealed the ratios of the configurational isomers for alkyl groups differing in bulkiness.

R	Bu^n	n-C_6H_{13}	Bu^i	Pr^i	$CHEt_2$	Me_3Si[4]
asym : *sym*	2.75 : 1	2.75 : 1	2.5 : 1	1.92 : 1	1.68 : 1	0 : 1

The ratio of the isomers (see above) substantially depends on the steric demands of the alkyl substituent: the content of the symmetric isomer is higher in the case of the bulkier substituent. In fact, the symmetric and asymmetric isomers of heptaphosphines may be treated in terms of products associated with thermodynamic and kinetic control, respectively.

Indeed, taking into account that the alkylation of heptaphosphide **1** involves sequential addition of organic substituents to all of the equatorial phosphorus atoms of the P_7 framework, we can assume that dialkylheptaphosphides **2** and **3** are intermediates in the formation of trialkylheptaphosphines **6** and **7**. Therefore, the asymmetric isomer of trialkylheptaphosphines *a*-**4**—*a*-**8** seems to form most rapidly and thus is a product of the kinetically controlled reaction.

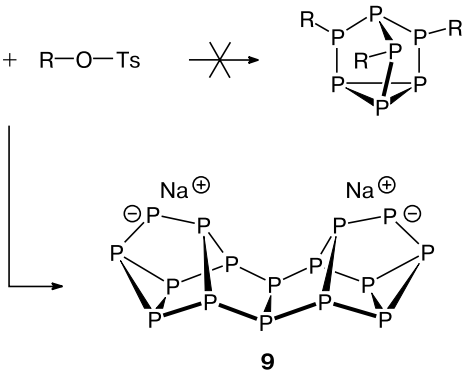
The symmetric isomers of heptaphosphines **6** and **7** can be obtained from the asymmetric isomers of dialkylheptaphosphides **2** and **3** only through inversion of an alkyl-bearing P atom, this process being characterized by a high energy barrier to activation. However, the symmetric isomer has a lower energy because of the whole system is sterically less strained. According to the foregoing, the symmetric isomer can be regarded as a product of the thermodynamically controlled reaction.

Proceeding further in these investigations, we found it interesting to study the reactivity of trisodium heptaphosphide toward tosylate derivatives of cyclic hydrocarbons with the aim of obtaining new heptaphosphines and revealing a variation in the ratio of the heptaphosphine isomers with the bulkiness of the substituent.

An example reaction of cyclohexyl tosylate with heptaphosphide **1** gave disodium hexadecaphosphide Na_2P_{16} (**9**) as the major product (Scheme 4). Analogous results were obtained in reactions of compound **1** with aryl tosylates.

Apparently, first heptaphosphide **1** reacts with cyclohexyl and aryl tosylates to give compounds of the $R_2P_7^-$ type, as in the aforementioned reactions of P_7^{3-} with acyclic alkyl tosylates. However, introduction of a third aryl group into $R_2P_7^-$ is sterically hindered. Being highly reactive, disubstituted heptaphosphides $R_2P_7^-$ are unstable and yield hexadecaphosphide **9** on decomposition; this has been demonstrated earlier with heptaphosphine derivatives as examples.[9,12]

Scheme 4



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R = *cyclo*-C_6H_{11}, *o*-MeC_6H_4, *p*-MeC_6H_4, *p*-$Bu^tC_6H_4$

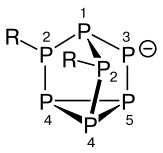
Thus, we discovered that the reactions of trisodium heptaphosphide (**1**) with alkyl tosylates provide an efficient and convenient route to dialkylheptaphosphides and trialkylheptaphosphines, while analogous reactions with cyclohexyl and aryl tosylates give disodium hexadecaphosphide as the major product.

Experimental

All manipulations for the preparation of the starting reagents, the synthesis and isolation of products were carried out in an inert atmosphere in standard Schlenk flasks. Solvents were used freshly distilled over Na/benzophenone. Trisodium heptaphosphide as an adduct with diglyme[13] and the starting tosylates were prepared according to known procedures: BuOTs,[14] $C_6H_{13}OTs$,[15] Pr^iOTs,[16] Bu^iOTs,[17] 3-$C_5H_{11}OTs$,[18] *cyclo*-$C_6H_{11}OTs$,[19] *o*-MeC_6H_4OTs,[20] *p*-MeC_6H_4OTs,[21] and *p*-$Bu^tC_6H_4OTs$.[22] NMR spectra were recorded on a Bruker MSL-400 instrument (400 (^1H) and 121.7 MHz (^{31}P)) with Me_4Si as the internal standard for ^1H and 85% H_3PO_4 as the external standard for ^{31}P. Mass spectra (EI, 50 eV, electron collector current 0.5 mA) were recorded on a Finnigan MAT-212 instrument. Exact mass values were determined against the reference peaks of perfluorokerosene.

Synthesis of sodium dialkylheptaphosphides (general procedure). Alkyl tosylate (2 equiv.) was added at −70 °C to a solution of trisodium heptaphosphide (**1**) in dry THF (10—20 mL). The reaction mixture was stirred at this temperature for 3 h and then at ~20 °C for 1 h. The yellow mixture turned red, producing small amounts of insoluble precipitates. They were filtered off, the solvent was removed, and the product was isolated from the resulting red-brown precipitate by extraction with toluene.

Sodium diisopropylheptaphosphide (2) was obtained from trisodium heptaphosphide (**1**) (1.2 g, 1.1 mmol) and isopropyl tosylate (0.47 g, 2.2 mmol). The yield was 0.48 g (74%), a red-brown powder. Found (%): C, 36.54; H, 7.08; P, 36.14. $C_{18}H_{42}NaO_6P_7$. Calculated (%): C, 36.36; H, 7.07; P, 36.53. ^1H NMR (THF-d_8), δ: 1.20 (m, 12 H, Me); 3.40 (m, 2 H, CH). ^{31}P NMR (THF-d_8), δ: 52 (dd, 2 P, P(2), $^1J_{P,P}$ = 364.43 Hz,

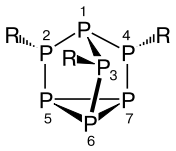


$^1J_{P,P}$ = 287.40 Hz); –46 (m, 1 P, P(1)); –124 (m, 1 P, P(5)); –129 (m, 1 P, P(3)); –163 (m, 2 P, P(4)) (the isomer *asym*-1).

Sodium diisobutylheptaphosphide (3) was obtained from trisodium heptaphosphide (**1**) (1.4 g, 1.3 mmol) and isobutyl tosylate (0.59 g, 2.6 mmol). The yield was 0.54 g (68%), a red-brown powder. Found (%): C, 38.05; H, 7.40; P, 35.54. $C_{20}H_{46}NaO_6P_7$. Calculated (%): C, 38.58; H, 7.39; P, 34.89. ^{1}H NMR (THF-d_8), δ: 0.89, 1.21 (both m, 6 H each, Me); 1.87 (m, 4 H, CH_2); 3.60 (m, 2 H, CH). ^{31}P NMR (THF), δ: 20 (dd, 2 P, P(2), $^1J_{P,P}$ = 339.25 Hz, $^1J_{P,P}$ = 279.99 Hz); –33 (m, 1 P, P(1)); –124 (m, 1 P, P(5)); –135 (m, 1 P, P(3)); –165 (m, 2 P, P(4)) (the isomer *asym*-1).

Synthesis of trialkylheptaphosphines 4—8 (general procedure). Alkyl tosylate (3 equiv.) was added at –70 °C to a solution of trisodium heptaphosphide (**1**) in dry THF (10—20 mL). The reaction mixture was stirred at this temperature for 3 h and then at ~20 °C for 1 h. The yellow mixture turned red; in some cases, insoluble precipitates were formed in small amounts. After filtration (when necessary) and removal of the solvent, the product was extracted from the resinous precipitate with toluene. The extract was filtered and concentrated to give individual trialkylheptaphosphine.

Tributylheptaphosphine (4) was obtained from trisodium heptaphosphide (**1**) (2.18 g, 2.1 mmol) and butyl tosylate (1.44 g, 6.3 mmol). The yield was 0.76 g (93%), a yellow oil. Found (%): C, 36.59; H, 6.92; P, 56.73. $C_{12}H_{27}P_7$. Calculated (%): C, 37.11; H, 6.96; P, 55.93. ^{1}H NMR (C_6D_6), δ: 0.85 (t, 9 H, MeCH$_2$, $^3J_{H,H}$ = 7.70 Hz); 1.36, 1.59 (both m, 6 H each, CH_2); 4.21 (m, 6 H, CH_2P). The *asym*-isomer: ^{31}P NMR (C_6D_6), δ: 115.81 (dddddd, 1 P, P(2), $^1J_{P(2),P(5)}$ = 358.1 Hz, $^1J_{P(2),P(1)}$ = 340.7 Hz, $^2J_{P(2),P(3)}$ = 62.22 Hz, $^2J_{P(2),P(4)}$ = 20.74 Hz, $^2J_{P(2),P(6)}$ = 17.78 Hz, $^2J_{P(2),P(7)}$ = 11.85 Hz); 84.73 (dddddd, 1 P, P(3), $^1J_{P(3),P(6)}$ = 331.8 Hz, $^1J_{P(3),P(1)}$ = 291.8 Hz, $^2J_{P(3),P(4)}$ = 174.81 Hz, $^2J_{P(2),P(3)}$ = 62.22 Hz, $^2J_{P(3),P(7)}$ = 17.78 Hz, $^2J_{P(3),P(5)}$ = 11.85 Hz); 16.41 (dddddd, 1 P, P(4), $^1J_{P(4),P(7)}$ = 268.14 Hz, $^1J_{P(4),P(1)}$ = 299.25 Hz, $^2J_{P(4),P(3)}$ = 174.81 Hz, $^2J_{P(4),P(2)}$ = 20.74 Hz, $^2J_{P(4),P(5)}$ = 32.6 Hz, $^2J_{P(4),P(6)}$ = 11.85 Hz); –78.84 (dddddd, 1 P, P(1), $^1J_{P(1),P(2)}$ = 340.7 Hz, $^1J_{P(1),P(3)}$ = 291.8 Hz, $^1J_{P(1),P(4)}$ = 299.25 Hz, $^2J_{P(1),P(5)}$ = 23.7 Hz, $^2J_{P(1),P(6)}$ = 32.6 Hz, $^2J_{P(1),P(7)}$ = 41.85 Hz); –120.62 (dddddd, 1 P, P(6), $^1J_{P(6),P(3)}$ = 331.8 Hz, $^1J_{P(6),P(5)}$ = 198.6 Hz, $^1J_{P(6),P(7)}$ = 235.55 Hz, $^2J_{P(6),P(1)}$ = 32.6 Hz, $^2J_{P(6),P(2)}$ = 17.85 Hz, $^2J_{P(6),P(4)}$ = 11.85 Hz); –161 (dddddd, 1 P, P(7), $^1J_{P(7),P(4)}$ = 268.14 Hz, $^1J_{P(7),P(5)}$ = 231.1 Hz, $^1J_{P(7),P(6)}$ = 235.55 Hz, $^2J_{P(7),P(1)}$ = 41.85 Hz, $^2J_{P(7),P(2)}$ = 11.85 Hz, $^2J_{P(7),P(3)}$ = 17.85 Hz); –173 (dddddd, 1 P, P(5), $^1J_{P(5),P(2)}$ = 358.1 Hz, $^1J_{P(5),P(6)}$ = 198.6 Hz, $^1J_{P(5),P(7)}$ = 231.1 Hz, $^2J_{P(5),P(1)}$ = 23.7 Hz, $^2J_{P(5),P(3)}$ = 11.85 Hz, $^2J_{P(5),P(4)}$ = 32.6 Hz). The *sym*-isomer: ^{31}P NMR (C_6D_6), δ: 77 (dd, 3 P, P(2), $^1J_{P(2),P(1)}$ = 331.84 Hz, $^1J_{P(2),P(3)}$ = 284.44 Hz); –104 (qq, 1 P, P(1), $^1J_{P(1),P(2)}$ = 331.84 Hz, $^2J_{P(1),P(3)}$ = 40.99 Hz); –161 (dd, 3 P, P(3), $^1J_{P(2),P(3)}$ = 284.44 Hz, $^2J_{P(1),P(3)}$ = 40.99 Hz).



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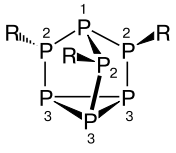

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Trihexylheptaphosphine (5) was obtained from trisodium heptaphosphide (**1**) (1.76 g, 1.7 mmol) and hexyl tosylate (1.3 g, 5.1 mmol). The yield was 0.76 g (95%), a yellow oil. Found (%): C, 46.08; H, 8.24; P, 45.57. $C_{18}H_{39}P_7$. Calculated (%): C, 45.76; H, 8.26; P, 45.97. ^{1}H NMR (C_6D_6), δ: 0.89 (t, 9 H, MeCH$_2$, $^3J_{H,H}$ = 7.57 Hz); 1.36 (m, 6 H, CH_2); 1.56—1.64 (m, 18 H, CH_2); 4.24 (m, 6 H, CH_2P). The *asym*-isomer: ^{31}P NMR (C_6D_6), δ: 115.68 (dddddd, 1 P, P(2), $^1J_{P(2),P(5)}$ = 361.5 Hz, $^1J_{P(2),P(1)}$ = 337.7 Hz, $^2J_{P(2),P(3)}$ = 62.22 Hz, $^2J_{P(2),P(4)}$ = 17.78 Hz, $^2J_{P(2),P(6)}$ = 26.67 Hz, $^2J_{P(2),P(7)}$ = 8.85 Hz); 84.61 (dddddd, 1 P, P(3), $^1J_{P(3),P(6)}$ = 331.84 Hz, $^1J_{P(3),P(1)}$ = 293.33 Hz, $^2J_{P(3),P(4)}$ = 174.81 Hz, $^2J_{P(2),P(3)}$ = 62.22 Hz, $^2J_{P(3),P(7)}$ = 17.78 Hz, $^2J_{P(3),P(5)}$ = 11.85 Hz); 16.39 (dddddd, 1 P, P(4), $^1J_{P(4),P(7)}$ = 266.66 Hz, $^1J_{P(4),P(1)}$ = 300.73 Hz, $^2J_{P(4),P(3)}$ = 174.81 Hz, $^2J_{P(4),P(2)}$ = 17.78 Hz, $^2J_{P(4),P(5)}$ = 35.55 Hz, $^2J_{P(4),P(6)}$ = 8.89 Hz); –78.84 (dddddd, 1 P, P(1), $^1J_{P(1),P(2)}$ = 337.7 Hz, $^1J_{P(1),P(3)}$ = 293.3 Hz, $^1J_{P(1),P(4)}$ = 300.7 Hz, $^2J_{P(1),P(5)}$ = 23.7 Hz, $^2J_{P(1),P(6)}$ = 32.6 Hz, $^2J_{P(1),P(7)}$ = 41.4 Hz); –120.67 (dddddd, 1 P, P(6), $^1J_{P(6),P(3)}$ = 331.84 Hz, $^1J_{P(6),P(5)}$ = 198.6 Hz, $^1J_{P(6),P(7)}$ = 235.55 Hz, $^2J_{P(6),P(1)}$ = 32.6 Hz, $^2J_{P(6),P(2)}$ = 26.7 Hz, $^2J_{P(6),P(4)}$ = 8.85 Hz); –161 (dddddd, 1 P, P(7), $^1J_{P(7),P(4)}$ = 266.66 Hz, $^1J_{P(7),P(5)}$ = 237.1 Hz, $^1J_{P(6),P(7)}$ = 235.55 Hz, $^2J_{P(7),P(1)}$ = 41.4 Hz, $^2J_{P(7),P(2)}$ = 8.85 Hz, $^2J_{P(7),P(3)}$ = 17.8 Hz); –173 (dddddd, 1 P, P(5), $^1J_{P(5),P(2)}$ = 361.5 Hz, $^1J_{P(5),P(6)}$ = 198.5 Hz, $^1J_{P(5),P(7)}$ = 237.0 Hz, $^2J_{P(5),P(1)}$ = 23.7 Hz, $^2J_{P(5),P(3)}$ = 11.8 Hz, $^2J_{P(5),P(4)}$ = 35.6 Hz). The *sym*-isomer: ^{31}P NMR (C_6D_6), δ: 77 (dd, 3 P, P(2), $^1J_{P(1),P(2)}$ = 331.84 Hz, $^1J_{P(2),P(3)}$ = 284.44 Hz); –104 (qq, 1 P, P(1), $^1J_{P(1),P(2)}$ = 331.84 Hz, $^2J_{P(1),P(3)}$ = 40.99 Hz); –161 (dd, 3 P, P(3), $^1J_{P(2),P(3)}$ = 284.44 Hz, $^2J_{P(1),P(3)}$ = 40.99 Hz).

Triisobutylheptaphosphine (6) was obtained from trisodium heptaphosphide (**1**) (2.9 g, 2.8 mmol) and isobutyl tosylate (1.9 g, 8.4 mmol). The yield was 1.03 g (96%), a yellow oil. Found (%): C, 37.6; H, 6.99; P, 55.36. $C_{12}H_{27}P_7$. Calculated (%): C, 37.11; H, 6.96; P, 55.93. ^{1}H NMR (THF-d_8), δ: 0.92 (m, 9 H, Me); 1.14 (m, 6 H, Me); 1.89 (m, 6 H, CH_2); 3.81 (m, 3 H, CH). The *asym*-isomer: ^{31}P NMR (C_6D_6), δ: 111.17 (dddddd, 1 P, P(2), $^1J_{P(2),P(5)}$ = 361.5 Hz, $^1J_{P(2),P(1)}$ = 333.8 Hz, $^2J_{P(2),P(3)}$ = 62.22 Hz, $^2J_{P(2),P(4)}$ = 20.74 Hz, $^2J_{P(2),P(6)}$ = 14.82 Hz, $^2J_{P(2),P(7)}$ = 11.85 Hz); 80.3 (dddddd, 1 P, P(3), $^1J_{P(3),P(6)}$ = 331.8 Hz, $^1J_{P(3),P(1)}$ = 291.8 Hz, $^2J_{P(3),P(4)}$ = 177.75 Hz, $^2J_{P(2),P(3)}$ = 62.22 Hz, $^2J_{P(3),P(5)}$ = 11.85 Hz, $^2J_{P(3),P(7)}$ = 17.78 Hz); 11.38 (dddddd, 1 P, P(4), $^1J_{P(4),P(7)}$ = 266.71 Hz, $^1J_{P(4),P(1)}$ = 300.74 Hz, $^2J_{P(4),P(3)}$ = 177.7 Hz, $^2J_{P(4),P(2)}$ = 20.74 Hz, $^2J_{P(4),P(5)}$ = 35.56 Hz, $^2J_{P(4),P(6)}$ = 11.85 Hz); –73.2 (dddddd, 1 P, P(1), $^1J_{P(1),P(2)}$ = 333.8 Hz, $^1J_{P(1),P(3)}$ = 291.8 Hz, $^1J_{P(1),P(4)}$ = 300.74 Hz, $^2J_{P(1),P(5)}$ = 20.7 Hz, $^2J_{P(1),P(6)}$ = 29.6 Hz, $^2J_{P(1),P(7)}$ = 41.5 Hz); –118 (dddddd, 1 P, P(6), $^1J_{P(6),P(3)}$ = 331.8 Hz, $^1J_{P(6),P(5)}$ = 198.6 Hz, $^1J_{P(6),P(7)}$ = 235.5 Hz, $^2J_{P(6),P(1)}$ = 29.6 Hz, $^2J_{P(6),P(4)}$ = 11.85 Hz, $^2J_{P(6),P(2)}$ = 14.81 Hz); –159 (dddddd, 1 P, P(7), $^1J_{P(7),P(4)}$ = 266.7 Hz, $^1J_{P(7),P(5)}$ = 231.1 Hz, $^1J_{P(7),P(6)}$ = 235.55 Hz, $^2J_{P(7),P(1)}$ = 41.5 Hz, $^2J_{P(7),P(2)}$ = 11.85 Hz, $^2J_{P(7),P(3)}$ = 17.78 Hz); –170.9 (dddddd, 1 P, P(5), $^1J_{P(5),P(2)}$ = 361.45 Hz, $^1J_{P(5),P(6)}$ = 198.6 Hz, $^1J_{P(5),P(7)}$ = 231.1 Hz, $^2J_{P(5),P(1)}$ = 20.7 Hz, $^2J_{P(5),P(3)}$ = 11.85 Hz, $^2J_{P(5),P(4)}$ = 35.56 Hz). The *sym*-isomer: ^{31}P NMR (C_6D_6), δ: 73.5 (dd, 3 P, P(2), $^1J_{P(1),P(2)}$ = 331.84 Hz, $^1J_{P(2),P(3)}$ = 284.44 Hz); –98 (qq, 1 P, P(1), $^1J_{P(1),P(2)}$ = 331.84 Hz, $^2J_{P(1),P(3)}$ = 40.99 Hz); –159 (dd, 3 P, P(3), $^1J_{P(2),P(3)}$ = 284.44 Hz, $^2J_{P(1),P(3)}$ = 40.99 Hz).

Triisopropylheptaphosphine (7) was obtained from trisodium heptaphosphide (**1**) (1.5 g, 1.44 mmol) and isopropyl tosylate (0.92 g, 4.32 mmol). The yield was 0.47 g (94%), a yellow oil. Found (%): C, 30.61; H, 6.05; P, 63.33. $C_9H_{21}P_7$. Calcu-

lated (%): C, 31.21; H, 6.07; P, 62.72. ^{1}H NMR (THF-d_8), δ: 0.96 (m, 18 H, Me); 3.54 (m, 3 H, CH). The *asym*-isomer: ^{31}P NMR (C_6D_6), δ: 140.3 (dddddd, 1 P, P(2), $^1J_{P(2),P(5)}$ = 373.31 Hz, $^1J_{P(2),P(1)}$ = 343.7 Hz, $^2J_{P(2),P(3)}$ = 56.3 Hz, $^2J_{P(2),P(4)}$ = 20.74 Hz, $^2J_{P(2),P(6)}$ = 14.81 Hz, $^2J_{P(2),P(7)}$ = 11.85 Hz); 105.78 (dddddd, 1 P, P(3), $^1J_{P(3),P(6)}$ = 346.66 Hz, $^1J_{P(3),P(1)}$ = 302.21 Hz, $^2J_{P(3),P(4)}$ = 162.96 Hz, $^2J_{P(2),P(3)}$ = 56.29 Hz, $^2J_{P(3),P(5)}$ = 11.85 Hz, $^2J_{P(3),P(7)}$ = 14.81 Hz); 38.7 (dddddd, 1 P, P(4), $^1J_{P(4),P(7)}$ = 279.99 Hz, $^1J_{P(4),P(1)}$ = 308.14 Hz, $^2J_{P(4),P(3)}$ = 162.96 Hz, $^2J_{P(4),P(2)}$ = 20.74 Hz, $^2J_{P(4),P(5)}$ = 32.6 Hz, $^2J_{P(4),P(6)}$ = 8.85 Hz); –88.46 (dddddd, 1 P, P(1), $^1J_{P(1),P(2)}$ = 343.7 Hz, $^1J_{P(1),P(3)}$ = 302.2 Hz, $^1J_{P(1),P(4)}$ = 308.14 Hz, $^2J_{P(1),P(5)}$ = 20.7 Hz, $^2J_{P(1),P(6)}$ = 29.6 Hz, $^2J_{P(1),P(7)}$ = 41.85 Hz); –120.62 (dddddd, 1 P, P(6), $^1J_{P(6),P(3)}$ = 346.6 Hz, $^1J_{P(6),P(5)}$ = 198.6 Hz, $^1J_{P(6),P(7)}$ = 235.5 Hz, $^2J_{P(6),P(1)}$ = 29.6 Hz, $^2J_{P(6),P(2)}$ = 14.85 Hz, $^2J_{P(6),P(4)}$ = 8.88 Hz); –161 (dddddd, 1 P, P(7), $^1J_{P(7),P(4)}$ = 279.99 Hz, $^1J_{P(7),P(5)}$ = 231.1 Hz, $^1J_{P(6),P(7)}$ = 235.55 Hz, $^2J_{P(7),P(1)}$ = 41.85 Hz, $^2J_{P(7),P(2)}$ = 11.85 Hz, $^2J_{P(7),P(3)}$ = 14.81 Hz); –176 (dddddd, 1 P, P(5), $^1J_{P(5),P(2)}$ = 373.31 Hz, $^1J_{P(5),P(6)}$ = 198.6 Hz, $^1J_{P(5),P(7)}$ = 231.1 Hz, $^2J_{P(5),P(1)}$ = 20.7 Hz, $^2J_{P(5),P(3)}$ = 11.85 Hz, $^2J_{P(5),P(4)}$ = 32.6 Hz). The *sym*-isomer: ^{31}P NMR (C_6D_6), δ: 103 (dd, 3 P, P(2), $^1J_{P(1),P(2)}$ = 297.77 Hz, $^1J_{P(2),P(3)}$ = 339.25 Hz); –115 (qq, 1 P, P(1), $^1J_{P(1),P(2)}$ = 297.77 Hz, $^2J_{P(1),P(3)}$ = 40 Hz); –161 (dd, 3 P, P(3), $^1J_{P(2),P(3)}$ = 339.25 Hz, $^2J_{P(1),P(3)}$ = 40 Hz).

Tri(3-pentyl)heptaphosphine (8) was obtained from trisodium heptaphosphide (**1**) (1.8 g, 1.73 mmol) and 3-pentyl tosylate (1.25 g, 5.19 mmol). The yield was 0.7 g (95%), a yellow oil. Found (%): C, 42.17; H, 7.66; P, 50.88. $C_{15}H_{33}P_7$. Calculated (%): C, 41.86; H, 7.67; P, 50.46. ^{1}H NMR (THF-d_8), δ: 0.86 (m, 18 H, Me); 1.82 (m, 12 H, CH_2); 3.79 (m, 3 H, CH). The *asym*-isomer: ^{31}P NMR (C_6D_6), δ: 133 (dddddd, 1 P, P(2), $^1J_{P(2),P(5)}$ = 385.18 Hz, $^1J_{P(2),P(1)}$ = 352.33 Hz, $^2J_{P(2),P(3)}$ = 57.7 Hz, $^2J_{P(2),P(4)}$ = 19.04 Hz, $^2J_{P(2),P(6)}$ = 10.06 Hz, $^2J_{P(2),P(7)}$ = 13.97 Hz); 95.56 (dddddd, 1 P, P(3), $^1J_{P(3),P(6)}$ = 355.61 Hz, $^1J_{P(3),P(1)}$ = 310.67 Hz, $^2J_{P(3),P(4)}$ = 170.58 Hz, $^2J_{P(2),P(3)}$ = 57.7 Hz, $^2J_{P(3),P(5)}$ = 15.36 Hz, $^2J_{P(3),P(7)}$ = 10.63 Hz); 25.7 (dddddd, 1 P, P(4), $^1J_{P(4),P(7)}$ = 292.13 Hz, $^1J_{P(4),P(1)}$ = 306.85 Hz, $^2J_{P(4),P(3)}$ = 170.58 Hz, $^2J_{P(4),P(2)}$ = 19.04 Hz, $^2J_{P(4),P(5)}$ = 31.42 Hz, $^2J_{P(4),P(6)}$ = 11.96 Hz); –84.48 (dddddd, 1 P, P(1), $^1J_{P(1),P(2)}$ = 352.33 Hz, $^1J_{P(1),P(3)}$ = 310.67 Hz, $^1J_{P(1),P(4)}$ = 306.85 Hz, $^2J_{P(1),P(5)}$ = 20.72 Hz, $^2J_{P(1),P(6)}$ = 42.02 Hz, $^2J_{P(1),P(7)}$ = 30.14 Hz); –120.92 (dddddd, 1 P, P(6), $^1J_{P(6),P(3)}$ = 355.61 Hz, $^1J_{P(6),P(5)}$ = 195.58 Hz, $^1J_{P(6),P(7)}$ = 234.98 Hz, $^2J_{P(6),P(1)}$ = 42.02 Hz, $^2J_{P(6),P(2)}$ = 10.06 Hz, $^2J_{P(6),P(4)}$ = 11.96 Hz); –166 (dddddd, 1 P, P(7), $^1J_{P(7),P(4)}$ = 292.13 Hz, $^1J_{P(7),P(5)}$ = 230.34 Hz, $^1J_{P(6),P(7)}$ = 234.98 Hz, $^2J_{P(7),P(1)}$ = 30.14 Hz, $^2J_{P(7),P(2)}$ = 13.97 Hz, $^2J_{P(7),P(3)}$ = 10.63 Hz); –175.6 (dddddd, 1 P, P(5), $^1J_{P(5),P(2)}$ = 385.18 Hz, $^1J_{P(5),P(6)}$ = 195.58 Hz, $^1J_{P(5),P(7)}$ = 230.34 Hz, $^2J_{P(5),P(1)}$ = 20.72 Hz, $^2J_{P(5),P(3)}$ = 15.36 Hz, $^2J_{P(5),P(4)}$ = 31.42 Hz). The *sym*-isomer: ^{31}P NMR (C_6D_6), δ: 91 (dd, 3 P, P(2), $^1J_{P(1),P(2)}$ = 345.42 Hz, $^1J_{P(2),P(3)}$ = 308.14 Hz); –113 (qq, 1 P, P(1), $^1J_{P(1),P(2)}$ = 345.42 Hz, $^2J_{P(1),P(3)}$ = 40.99 Hz); –163.2 (dd, 3 P, P(3), $^1J_{P(2),P(3)}$ = 308.14 Hz, $^2J_{P(1),P(3)}$ = 40.99 Hz).

Reaction of trisodium heptaphosphide (1) with cyclohexyl tosylate. Cyclohexyl tosylate (1.4 g, 5.4 mmol) was added at –70 °C to a solution of trisodium heptaphosphide (**1**) (2.0 g, 1.8 mmol) in dry THF (15 mL). The reaction mixture was stirred at this temperature for 3 h and then at ~20 °C for 1 h. The yellow mixture turned faintly red. The yield of disodium hexadecaphosphide Na_2P_{16} (**9**) was 0.19 g (46%), a red powder. ^{31}P NMR (DMF), δ: 60 (m, 4 P); 38 (m, 2 P); 6 (m, 2 P); –34 (m, 2 P); –134 (m, 2 P); –172 (m, 4 P). MS, found: *m/z* 541.5598 $[M]^+$. Na_2P_{16}. Calculated: M = 541.5598.

Reaction of trisodium heptaphosphide (1) with 2-methylphenyl tosylate. Disodium hexadecaphosphide Na_2P_{16} (**9**) was also obtained from trisodium heptaphosphide (**1**) (1.8 g, 1.65 mmol) and 2-methylphenyl tosylate (1.3 g, 4.95 mmol). The yield was 0.18 g (46% to the consumed phosphorus), red crystals. ^{31}P NMR (DMF), δ: 60 (m, 4 P); 38 (m, 2 P); 6 (m, 2 P); –34 (m, 2 P); –134 (m, 2 P); –172 (m, 4 P). MS, found: *m/z* 541.5598 $[M]^+$. Na_2P_{16}. Calculated: M = 541.5598.

Reaction of trisodium heptaphosphide (1) with 4-methylphenyl tosylate. Disodium hexadecaphosphide Na_2P_{16} (**9**) was also obtained from trisodium heptaphosphide (**1**) (2.1 g, 1.9 mmol) and 4-methylphenyl tosylate (1.5 g, 5.7 mmol). The yield was 0.2 g (43% to the consumed phosphorus), red crystals. ^{31}P NMR (DMF), δ: 60 (m, 4 P); 38 (m, 2 P); 6 (m, 2 P); –34 (m, 2 P); –134 (m, 2 P); –172 (m, 4 P). MS, found: *m/z* 541.5598 $[M]^+$. Na_2P_{16}. Calculated: M = 541.5598.

Reaction of trisodium heptaphosphide (1) with 4-*tert*-butylphenyl tosylate. Disodium hexadecaphosphide Na_2P_{16} (**9**) was also obtained from trisodium heptaphosphide (**1**) (1.9 g, 1.7 mmol) and 4-*tert*-butylphenyl tosylate (1.6 g, 5.1 mmol). The yield was 0.2 g (48% to the consumed phosphorus), red crystals. ^{31}P NMR (DMF), δ: 60 (m, 4 P); 38 (m, 2 P); 6 (m, 2 P); –34 (m, 2 P); –134 (m, 2 P); –172 (m, 4 P). MS, found: *m/z* 541.5598 $[M]^+$. Na_2P_{16}. Calculated: M = 541.5598.

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References

1. V. A. Milyukov, Yu. G. Budnikova, and O. G. Sinyashin, *Usp. Khim.*, 2005, **74**, 859 [*Russ. Chem. Rev.*, 2005, **74**, 781 (Engl. Transl.)].
2. H. G. von Schnering and W. Hönle, *Chem. Rev.*, 1988, **88**, 243.
3. M. Baudler and K. Glinka, *Chem. Rev.*, 1993, **93**, 1623.
4. G. Fritz, K. D. Hoppe, W. Hönle, D. Weber, C. Mujica, and H.-G. von Schnering, *J. Organomet. Chem.*, 1983, **249**, 63.
5. M. Baudler, W. Faber, and J. Hahn, *Z. Anorg. Allg. Chem.*, 1980, **469**, 15.
6. G. Fritz and H.-W. Schneider, *Z. Anorg. Allg. Chem.*, 1990, **584**, 12.
7. S. Charles, J. C. Fettinger, and B. W. Eichhorn, *J. Am. Chem. Soc.*, 1995, **117**, 5303.
8. A. M. R. Gonsalves, J. C. Bayon, M. E. S. Serra, and J. P. R. Pereira, *J. Organomet. Chem.*, 1998, **553**, 199.
9. G. Fritz, H. Rothmann, and E. Matern, *Z. Anorg. Allg. Chem.*, 1992, **610**, 33.
10. K. Marat, *SPINWORKS, Ver. 2.3*, University of Manitoba, Canada, 2004.

11. *PERCH, Ver. 1*, PERCH Solutions Ltd., Kuopio (Finland), 2005.
12. M. Baudler, R. Heumüller, and J. Hahn, *Z. Anorg. Allg. Chem.*, 1985, **529**, 7.
13. V. A. Milyukov, A. V. Kataev, O. G. Sinyashin, and E. Hey-Hawkins, *Izv. Akad. Nauk, Ser. Khim.*, 2006, 1249 [*Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 1297].
14. H. Gilman and O. L. Marrs, *J. Org. Chem.*, 1965, **30**, 2096.
15. C. H. Snyder and A. R. Sotto, *J. Org. Chem.*, 1964, **29**, 742.
16. K. M. Davies and W. J. Hickinbottom, *J. Chem. Soc.*, 1965, **3**, 2295.
17. G. M. Fraser and H. M. R. Hoffman, *J. Chem. Soc. B*, 1967, **5**, 425.
18. D. L. Tabern and E. H. Volwiler, *J. Am. Chem. Soc.*, 1934, **56**, 1139.
19. D. J. McLenan, *J. Chem. Soc. B*, 1966, **28**, 705.
20. J. M. Tedder and B. Webster, *J. Chem. Soc.*, 1960, **11**, 4417.
21. M. Neeman, A. Modiano, and Y. Shor, *J. Org. Chem.*, 1956, **21**, 671.
22. D. Zim, V. R. Lando, and J. Dupont, *Org. Lett.*, 2001, **3**, 3049.

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