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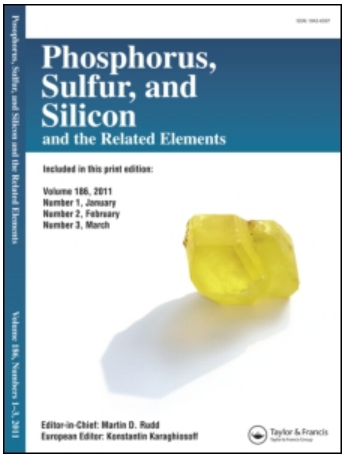

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AN IMPROVED PREPARATION OF TRIS(TRIMETHYLSILYL)HEPTAPHOSPHINE

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AN IMPROVED PREPARATION OF TRIS(TRIMETHYLSILYL)HEPTAPHOSPHINE

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The title compound is available in a non-hazardous, high-yield two-step procedure. Tri(sodium/potassium)heptaphosphide is prepared from red phosphorus and the liquid Na/K alloy in boiling monoglyme, and reacted further with chlorotrimethylsilane in toluene at −50°C to give an 80% isolated yield of $(Me_3Si)_3P_7$.

Key words: Polyphosphines, silyl-; polyphosphides, silyl-; heptaphosphine, tris(trimethylsilyl)heptaphosphine.

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INTRODUCTION

The tricyclic cage of the heptaphosphide(3-) anion is a fascinating structural unit both for solid state and molecular chemistry.[1–16] In its molecular derivatives R_3P_7 it features a C_3 or C_{3v} symmetrical structure (related to the structure of P_4S_3) which is not fluctional in solution, contrary to the situation with the heptaphosphide(3-) anion.[6–8] A variety of side-groups R can be introduced, among which the trimethylsilyl group is of prime importance.[1–6,9–11] This silylated derivative shows satisfactory stability, is easily purified, and is a valuable synthon for other P_7-based compounds due to the pronouncedly regioselective (Si—P) reactivity. However, the synthetic procedures proposed for this compound in the literature are not really very satisfactory. In all of these preparations large amounts of white phosphorus and alkali metal have been used, which makes the processes hazardous and unpleasant when carried out in larger quantities, which is necessary owing to the lower overall yields. The latter arise from the formation of various by-products which lead to severe separation problems.

In the course of work on gold(I) polyphosphides we have become interested in $(Me_3Si)_3P_7$ as a starting material and have therefore decided to develop a more efficient and less hazardous procedure. It turned out that significant improvements of the conventional synthesis can be accomplished 1) by using cheap and non-inflammable red phosphorus (instead of white phosphorus), 2) by using cheap sodium and potassium metal alloy (instead of lithium or its alkyls) and 3) by working in toluene as a solvent (instead of ethers, glymes or tetrahydrofuran) in the silylation step. In summary the preparation which we are now able to describe below is less dangerous, less costly and more efficient than the previous procedures.

RESULTS

Tris(trimethylsilyl)heptaphosphine is conveniently prepared following the procedure given in Equations 1 and 2:

$$7P_{red} + 3Na/K\ (glyme) \rightarrow (Na/K)_3P_7 \quad (1)$$

$$(Na/K)_3P_7 + 3Me_3SiCl\ (toluene) \rightarrow (Me_3Si)_3P_7 + 3Na/KCl \quad (2)$$

The crystalline product is obtained in an overall 80% isolated yield and is readily identified by its physical and spectral properties.

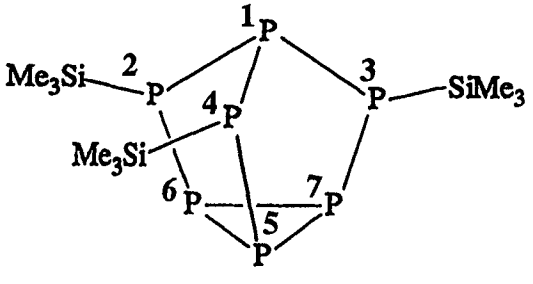
EXPERIMENTAL

Preparation of Tris(trimethylsilyl)heptaphosphine: In a dry 250 mL round bottom three-necked flask purged with dry nitrogen a liquid alloy is formed from sodium (1.32 g, 57 mmol) and potassium (1.69 g, 42 mmol) by gentle heating. After cooling this alloy is covered with dry monoglyme and the solvent is heated to reflux temperature for 2 h under nitrogen. The colour of the solvent turns to a lasting deep blue. After cooling to room temperature red phosphorus powder is added (5.67 g, 183 mmol) and the mixture is again heated to reflux for 24 h. The solvent is then removed from the yellowish-green suspension in a vacuum at ambient temperature. The weight of the remaining product is the sum of the weights of the reagents, which corresponds to a 25% excess of alkali metal relative to the amount of phosphorus as related to a tri(mixed-metal) heptaphosphide M_3P_7.

This phosphide is crushed and suspended in dry toluene (150 mL) with mechanical stirring under nitrogen at room temperature, and then cooled to −50°C. Over a period of 30 min chlorotrimethylsilane is added (14 mL, 109 mmol, excess), and stirring is continued for 5 h at −50°C before the mixture is allowed to warm to ambient temperature, filtered, and washed with dry hexane (40 mL). The volume of the combined filtrates is reduced to ca. 75 mL, and the clear yellow liquid is slowly cooled to −30°C. A colourless crystalline product separates in a total yield of 8.9 g (78%), m.p. 140°C.

$C_9H_{27}P_7Si_3$ (436.39)	Calcd.	C 24.77, H 6.24, P 49.68, Si 19.31
	Found	C 24.53, H 6.49, P 49.29, Si 19.45

^1H NMR (C_6D_6, 25°C): δ = 0.22, s, Me. $\{^1H\}^{13}C$ NMR (v.s.): δ = 3.60, s, Me. $\{^1H\}^{29}Si$ NMR (v.s.): δ = 7.70, dm, ^1J(SiP) = 39.4 Hz, $SiMe_3$. $\{^1H\}^{31}P$ NMR (v.s.): δ = 0.0, m, 3P, $P_{2,3,4}$; −99.4, qq, ^1J(P, P) = −325.1 Hz, ^2J(P, P) = 44.6 Hz, 1P, P_1; −156.9, m, 3P, $P_{5,6,7}$.



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