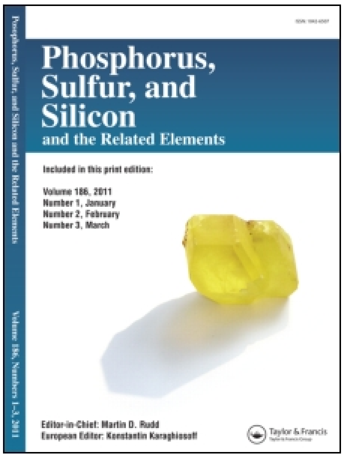

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A PHOSPHORANE WITH A (λ^5)-PHOSPHORUS—SILICON BOND

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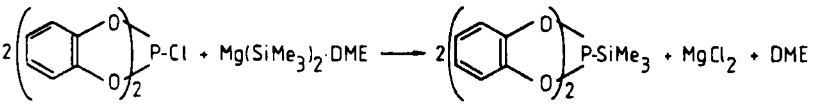
Reaction of bis(trimethylsilyl)magnesium with bis(catechyl)chlorophosphorane has furnished the first phosphorane with a (λ^5)-phosphorus—silicon bond, extending the range of atoms known to give rise to stable phosphoranes when bonded to five-co-ordinate phosphorus. The novel phosphorane has been characterized by analysis, n.m.r. spectra and from its mass spectrum.

After phosphorus pentafluoride, PF_5 had been in the literature since the late 19th century[1] its pentaphenyl derivative, PPh_5 was the first compound to be referred to as a so-called phosphorane in 1949.[2] In the meantime an enormous variety of phosphoranes, molecular species involving five-co-ordinate (λ^5) phosphorus, have been synthesized and were investigated structurally (c.f., e.g.,[3–5]). A specific class of compounds which has attracted considerable interest during the past 25 years is that of the fluorophosphoranes, R_nPF_{5-n} (R = hydrocarbon group; $n = 1$, 2, or 3) which contain carbon and phosphorus directly and simultaneously bonded to λ^5 phosphorus. Compounds belonging to this class are particularly amenable to structural studies using n.m.r. spectroscopy (especially ^{19}F and ^{31}P).[6]

It has emerged at an early stage that the introduction of "heteroatoms" into fluorophosphoranes causes notable effects with regard to the dynamic and static stereochemistry of these compounds (for which the trigonal-bipyramidal (TBP) structure has been found to be prevailing[3–6]). Typical cases in point are fluorophosphoranes with nitrogen- (e.g. R_2NPF_4, R_2NPF_3R', $R_2NPF_2R'_2$),[7–9] oxygen-,[10–12], or sulfur- (e.g. $RSPF_4$, $RSPF_3R'$, $RSPF_2R'_2$)-containing substituents.[13,14] Phosphoranes and fluorophosphoranes with lower-valent (λ^3) phosphorus directly bonded to λ^5-phosphorus have recently become available.[15–20] A number of atoms at five-coordinate phosphorus are now known to occur in phosphoranes, affecting the chemistry and stereochemistry of these species.

We now wish to report a further extension of the range of heteroatom-containing substituents at λ^5-phosphorus as realized in the synthesis of a novel type of compound, bis(catechyl)trimethylsilyl phosphorane, **3**. The starting material was a long-known chlorophosphorane, $(C_6H_4O_2)_2PCl$, **1**,[21] which was allowed to react with a novel reagent, $Mg(SiMe_3)_2 \cdot DME$ (DME = dimethoxyethane), **2** which is known to be capable of transferring trimethylsilyl groups. This reagent was first synthesized simultaneously in 1977 by Oliver and his co-workers,[22] and by Rösch.[23] The laborious, low-yield preparation of the reagent prevented its extensive use in synthetic chemistry, and only a substantial improvement of the synthesis of both the precursor, $Hg(SiMe_3)_2$,[24] and of the silyl-magnesium compound itself[25] led to bis(trimethylsilyl)magnesium becoming available as a readily accessible, unusual silylating agent. It could soon be demonstrated that the reagent permits the synthesis of compounds which are not (or only with difficulty) accessible by the use of other silylating agents. Using $Mg(SiMe_3)_2 \cdot DME$, **2** it was possible, for example, to synthesize the first organosilyl-lead compound, $Pb(SiMe_3)_4$,[26] and also one of the first persilylated transition metal compounds, $Fe(SiMe_3)_3 \cdot THF$.[27]

These observations encouraged us to apply **2** as a reagent to the synthesis of the first λ^5P—Si-bonded phosphorane, $(C_6H_4O_2)_2(Me_3Si)P$, **3**, via



1 **2** **3**

The reagent, **2**, was applied in an excess of 25%, relative to the stoichiometric quantity of **1**, and the reaction was conducted by the addition of **1** to a solution of **2** in pentane at −28°C. The novel phosphorane, **3** was obtained in relatively low yield, ca. 20%. The other products of the reaction are not known but it is thought that the low yield is due to the reagent **2** attacking not only at the P—Cl bond of **1** but also at the oxygen atoms.

The phosphorane, **3** is a solid well to moderately soluble in organic solvents. It is stable in air for short periods; solutions in toluene are stable up to 70°C. Elemental analysis and the high resolution mass spectrum are consistent. N.m.r. spectra were recorded for the nuclei, ^1H, ^{13}C, and ^{31}P, as follows: ^1H (TMS): 0.24 (d); $^3J((C\underline{H}_3)_3Si—\underline{P})$ 2.4; 6.7–7.1 (m); ^{13}C (TMS; spin-decoupled from ^1H): 0.32 (s); 113–125 (m); The integrated ^1H and ^{13}C n.m.r. spectra were consistent. ^{31}P (85% H_3PO_4; spin-decoupled from ^1H): −132.64 (s).

Our observations serve to establish the existence of a novel (λ^5P)-trimethylsilylphosphorane involving a direct bond between silicon and (λ^5) phosphorus. A study of the reactivity of compound **3** at the silicon-phosphorus bond should reveal interesting chemistry. A crystal structure determination of the novel phosphorane would clearly be desirable but attempts at growing suitable crystals, employing various conditions and solvents, have failed, thus far.

EXPERIMENTAL

All experiments were conducted with careful exclusion of air and moisture. Purified argon was employed as a protective gas.

N.m.r. spectra: ^1H and ^{13}C, Bruker WP 80 SY; ^{31}P, Bruker, SXP 4-100. Solvent: Deuterio-tetrahydrofuran. Mass spectrum: Varian MAT 311 A.

Preparation of **3**. A solution of **2** (2.61 g; 0.01 mol) in 60 mL of pentane was cooled to −28°C. The chlorophosphorane, **1** (4.5 g; 0.016 mol; molar ratio **1** : **2** = 1 : 1.6) was added in small portions over a period of 5 min. The solution was found to assume a yellow coloration, and was stirred for 3 d, was allowed to warm up to 0°C, and was stirred for a further 4 d. Solids were allowed to settle, and the supernatant liquid was decanted. In order to remove unreacted **2** the yellow residue was washed with two 30 mL portions of pentane. The residue thus left was pumped dry, and was extracted at 70°C with three 30 mL portions of toluene. The combined extracts were concentrated in the vacuum of an oil-pump. Upon storage over 24 h in a low-temperature refrigerator 0.95 g (18.5%) of **3** as fine, yellow needles were precipitated.

The phosphorane **3** was found to be well soluble in THF, moderately soluble in ether and toluene, slightly soluble in benzene, and nearly insoluble in pentane. The m.p. (with partial decomposition) was observed at 142°C. Anal. (320.35); found, C, 55.84; H, 5.78; calc., C, 56.24; H, 5.78.

Mass Spectrum: the fragmentation was consistent with the expectation. The isotopic distribution for the molecular peak was found in agreement with calculation. High resolution for the molecular peak, calc. 320.0634; found, 320.0632.

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