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2,4,6-TRI-*tert*-BUTYLPHENYLPHOSPHENE-DIMESITYLSILENE;
THE FIRST PHOSPHASILAALKENE

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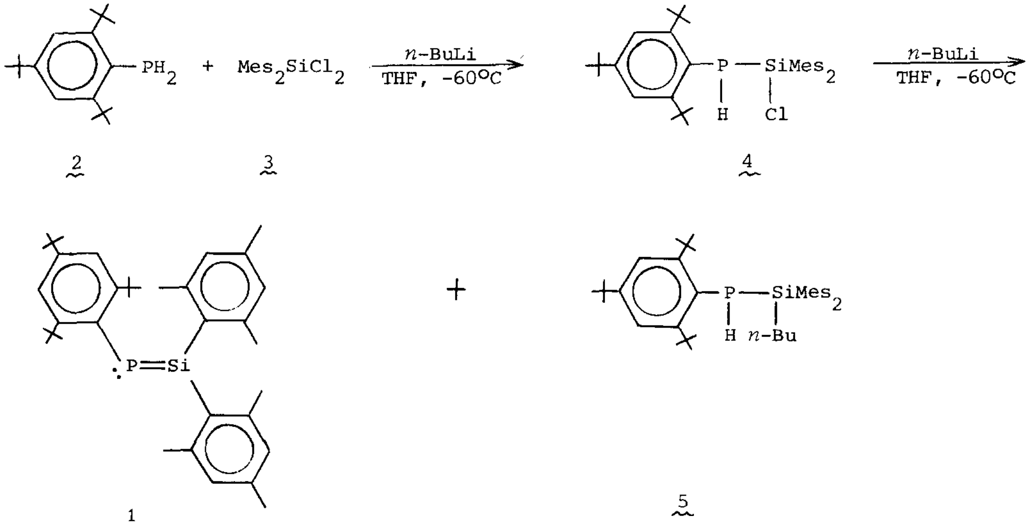
Abstract: The title compound (1) was prepared from chlorodimesitylsilyl-2,4,6-tri-*tert*-butylphenylphosphine (4) with *n*-butyllithium and characterized by its spectral data and by its chemical conversion with methanol to the adduct 6.

The field of hetero- and diheteroalkenes containing heavier heteroelements has shown a rapid and impressive development in recent years. Originally believed to be unstable (confer the so-called Double Bond Rule[1]), an increasing number of such compounds could be prepared if suitably protected, in particular by bulky substituents[2]. In general, their stability has been found to decrease for the lower Groups and for the higher Periods, i.e. towards the left and bottom of the Periodic Table. Milestones in this respect are the disilenes (RR'Si=SiRR')[2g] and a phosphastibaalkene (RP=SbR')[2e]. We wish to report a novel borderline case containing the highly reactive P=Si double bond, 2,4,6-tri-*tert*-butylphenylphosphene-dimesitylsilene (1) (Scheme 1). The compound has been prepared in solution, but due to its high reactivity, it has so far not been isolated in pure form.

Scheme 1



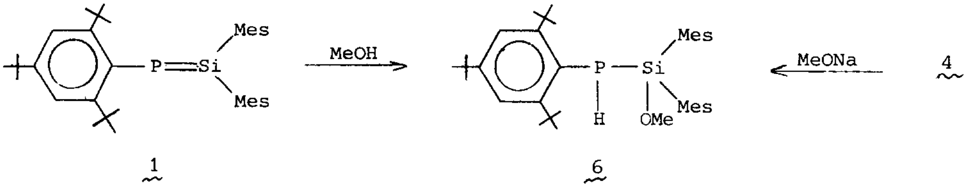
The reaction of equimolar quantities of **2**[3] and **3**[4] (dissolved in THF) with one equivalent of *n*-butyllithium (dissolved in hexane) at -60°C, followed by warming to room temperature, afforded **4** which was isolated by evaporation of the solvent and extraction of **4**[5] with pentane. Under nitrogen, with extreme exclusion of air and moisture, one equivalent of *n*-butyllithium in hexane was added slowly at -60°C to the solution of **4** in THF; a deep red colour developed (presumably that of $ArPLiSiClMes_2$). On warming to room temperature, the colour changed to orange. According to ^{31}P NMR spectroscopy, **1** and **5**[6] were the only phosphorus-containing compounds in solution (about 50% each). Although **1** was relatively long-lived in the reaction mixture ($t_{\frac{1}{2}}$ ca. 1 day at 25°C; ca. 1 week at -60°C), it instantaneously and completey decomposed on admission of minute amounts of air; this high reactivity so far thwarted all attempts to isolate or purify it. The structural assignment is therefore mainly based on spectroscopic data.

The ^{29}Si NMR spectrum provides the strongest evidence with a signal at the very low field shift of δ = + 76.7 ppm (THF). Such low field chemical shifts are quite rare in organosilicon compounds[7], but are typically observed for tricoordinate, pπ-hybridized silicon (41.4 to 94 ppm) [2f,g]. Similarly, the coupling constant $^1J(PSi)$= 148.5 Hz is unusually high; for tetracoordinate silicon, values above 100 Hz have not been observed[7] with the exception of $LiP(SiH_3)_2$ ($^1J(PSi)$= 256 Hz) [9]. Both δ and J strongly suggest that silicon is involved in pπ--bonding.

Much to our surprise and even distress, the situation was not so clear-cut for the ^{31}P NMR spectrum. We had expected a chemical shift of approximately + 300 ppm by the following extrapolation. From -P=N-(δ ca. 475 ppm[2b]) to -P=P-(δ ca. 500 ppm[2c]), δ increases approximately 25 ppm, a tendency which continues for the heavier elements (-P=As: δ ca. 575 ppm[2e]; -P=Sb-: δ= 620 ppm[2e]). In analogy, one might have guessed that the replacement of carbon in the -P=C unit by silicon would be accompanied by a comparable downfield shift (triarylphosphaalkenes typically resonate in the range of δ= 200-280 ppm[2a]). However, the actual value for **1** was found at δ= 136.0 ppm (THF; $^1J(PSi)$= 148.5 Hz; no P-H coupling observed). Although this shift to relatively high field is unexpected and unexplained, it is, on the other hand, in line with electronegativity considerations (χ_C= 2.5; χ_{Si}= 1.8); a high field shift is actually observed when a P-C single bond is replaced by the corresponding P-Si bond. Further investigations are necessary to clarify wich factors are responsible for this interesting dichotomy of chemical shift behaviour of two-coordinated phosphorus when bound to Group V or to Group IV elements, respectively.

The structure of **1** was further corroborated by its chemical transformation with methanol to **6** (Scheme 2). The reaction was performed by addition of an excess of methanol to the previously mentioned solution containing **1** and **5**. Not surprisingly, **5** was unaffected, but the ^{31}P NMR signal of **1** (δ= 136 ppm) was immediately replaced by that of **6** (δ= -112.6 ppm, $^1J(PH)$= 219 Hz). The identity of **6**[10] was proven by its independent synthesis from **4** with sodium methoxide in methanol.

Scheme 2



The addition of methanol to **1** is highly regiospecific; the regioisomer **7** ($ArP(OMe)SiHMes_2$) of **6** was not present according to the ^{31}P NMR spectrum (there was a negligible signal of an unidentified compound at $\delta = 23$ ppm which might be due to traces of **7**). The regiochemistry is obviously determined by polar effects. Silicon ($\chi = 1.8$) is more electropositive than phosphorus ($\chi = 2.1$), and therefore the P=Si bond is expected to be highly polarized with silicon as the positive pole to which the nucleophilic component of a polar reactant molecule will add. A similar situation has previously been encountered for phosphaalkenes[11] in which the P=C bond is polarized due to a comparable difference in electronegativity between the two constituting atoms phosphorus and carbon; an obvious difference between phosphaalkenes and phosphasilaalkenes resides, of course, in the direction of the polarization with phosphorus being the positive pole of the P=C bond and the negative pole of the P=Si bond.

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5. **4**: ^{1}H NMR (CDCl$_3$, δ in ppm): 7.24 (bs, 2H, aryl H of (t-Bu)$_3$C$_6$H$_2$), 6.69 (s, 4H, aryl H of Mes), 5.02 (d ,1H, ^{1}J(PH)= 223 Hz, PH), 2.21 (s, 6H, p-CH$_3$), 2.14 (s, 12H, o-CH$_3$), 1.31 (bs, 27H, t-Bu). ^{31}P NMR (CDCl$_3$, δ in ppm): -106 (d, ^{1}J(PH)= 224 Hz). ^{29}Si NMR: (CDCl$_3$, δ in ppm): 8.9 (d, ^{1}J(PSi)= 58 Hz). Mass spectrum (m/z (%)): 578 (37) M$^{+\cdot}$, 301 (58) SiMes$_2$Cl^{+}, 277 (51) Bu$_3$C$_6$H$_2$PH^{+}, 231 (100); C$_{36}$H$_{52}$ClPSi, calcd. 578.3188, found 578.3173.

6. **5**: ^{1}H NMR (CDCl$_3$, δ in ppm): 7.17 (bs, 2H, aryl H of (t-Bu)$_3$C$_6$H$_2$), 6.69 (s, 4H, aryl H of Mes), 4.63 (d, 1H, ^{1}J(PH)= 217 Hz, PH), 2.20 (s, 6H, p-CH$_3$), 1.94 (s, 12H, o-CH$_3$), 1.40-0.60 (m, 9H, n-Bu), 1.31 (bs, 27H, t-Bu). ^{31}P NMR (THF, δ in ppm): -116.6 (d, ^{1}J(PH)= 216 Hz). Mass spectrum (m/z (%)): 600 (2.9) M$^{+\cdot}$, 323 (89) SiMes$_2$Bu^{+}, 277 (6) Bu$_3$C$_6$H$_2$PH^{+}, 267 (100) SiHMes$_2$$^{+}$; C$_{40}H_{61}$PSi, calcd. 600.4280, found 600.4288.

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10. **6**: ^{1}H NMR (CDCl$_3$, δ in ppm), 7.17 (d, 2H, ^{4}J(PH)= 2 Hz, aryl H of (t-Bu)$_3$C$_6$H$_2$), 6.65 (s, 4H, aryl H of Mes), 4.62 (d, 1H, ^{1}J(PH)= 220 Hz, PH), 3.15 (s, 3H, OCH$_3$), 2.20 (s, 6H, p-CH$_3$), 2.02 (s, 12H, o-CH$_3$), 1.35 (s, 18H, ortho-t-Bu), 1.30 (s, 9H, para-t-Bu). ^{31}P NMR (THF, δ in ppm): -112.6 (d, ^{1}J(PH)= 219 Hz). Mass spectrum (m/z (%)): 574 (7.5) M$^{+\cdot}$, 325 (21), 297 (100) SiMes$_2$OCH$_3$$^{+}$, 277 (35) Bu$_3C_6H_2$PH^{+}; C$_{37}H_{55}$OPSi, calcd. 574.3589, found 574.3560.

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