Some [tris(trimethyl)- and [tris(dimethylphenyl)-silyl]methyl derivatives of phosphorus. The crystal structure of [tris(dimethylphenylsilyl)methylphosphonous dichloride

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Abstract

The compounds $TsiPCl_2$ (Tsi = $(Me_3Si)_3C$) (I), and $TpsiPCl_2$ (Tpsi = $[(PhMe_2Si)_3C]$) (II), have been obtained by the reaction of TsiLi or TpsiLi with PCl_3. In the case of TsiLi the reaction conditions could be varied so that 50% yields of the diphosphene TsiP=PTsi were obtained instead of compound I. Reaction of TsiLi with PBr_3 gave mainly TsiBr along with a little $TsiPBr_2$, but the latter was obtained in high yield by treatment of I with BBr_3. TpsiLi did not react with PPh_2Cl, but with $PPhCl_2$ gave TpsiCl. Reaction of TsiLi with $P(O)Cl_3$ gave TsiCl. The halides TsiX and TpsiX (X = Cl or Br) were made independently in ca. 50% yield from TsiLi or TpsiLi and the halides CX_4. With $P(OMe)_3$, TsiLi gave TsiMe in good yield, rather than $TsiP(OMe)_2$, but the latter was obtained by treatment of I with MeOH containing NaOMe; with MeOH alone I gave $(Me_3Si)_2CHP(OMe)_2$. Reaction of I with $AgNO_3$ gave $TsiP(O)Cl_2$, which on treatment with MeOH containing pyridine gave $(Me_3Si)_2CHP(O)(OMe)_2$. Reaction of II with $LiAlH_4$ gave $TpsiPH_2$, and reaction of I with $NaBH_4$ gave the adduct $TsiPH_2 \cdot BH_3$. The identity of II has been confirmed by an X-ray diffraction study which shows that the crystals consist of discrete molecules with P–Cl 2.087(9) Å and Cl–P–Cl 96.1(1)°.

Introduction

Much novel chemistry has emerged from studies of organophosphorus compounds in which the bulky tris(trimethylsilyl)methyl group, $(Me_3Si)_3C$, (frequently denoted below by Tsi) is attached to phosphorus. In particular, compounds of the type $(Me_3Si)_3CPRCl$ have been found to lose Me_3SiCl on heating to give more or less stable phosphaalkenes $(Me_3Si)_2C=PR$ [1]. (When R = Cl, further heating gives $(Me_3SiC≡P)_x$). Furthermore, treatment of $TsiPCl_2$ with sodium naphthalene, TsiLi, or t-BuLi gives the stable diphosphene TsiP=PTsi [2–4]; the same compound has

been obtained by treatment of TsiP(Cl)–P(Cl)Tsi with t-BuLi [3]. The diphosphene $(Me_3Si)_2CHP=PAr$ (Ar = 2,4,6-$Bu^t_3C_6H_2$) has been made by treatment of a mixture of $TsiPCl_2$ and $ArPH_2$ with 1,8-diazabicyclo[5.4.0]undec-7-ene) [5]. Reaction of TsiLi with $(Me_3Si)_2C=PCl$ has given the phosphaalkene $TsiP=C(SiMe_3)_2$ [6], and treatment of a mixture of $TsiPCl_2$ and $TsiAsCl_2$ with t-BuLi has given TsiP=AsTsi [7].

A noteworthy feature of the chemistry of $TsiPCl_2$ is that it may be recrystallised from MeOH [8]. In contrast, the compound $TsiPPh_2$ was found to be unstable towards MeOH, losing its Me_3Si groups successively, to give ultimately $MePPh_2$. Protonation at phosphorus is apparently followed by nucleophilic attack by the solvent at silicon; no reaction occurs when NaOMe is present because this inhibits the protonation [9].

We describe here some further studies of compounds in which a phosphorus atom bears the Tsi group or the related group $(Me_2PhSi)_3C$, denoted by Tpsi: $TsiPCl_2$ (I, $(Me_3Si)_3C$ = Tsi); $TpsiPCl_2$ (II, $(Me_2PhSi)_3C$ = Tpsi).

Results and discussion

We made $TsiPCl_2$ (I) in good yield by adding a solution of TsiLi in THF to a solution of PCl_3 in Et_2O at room temperature (cf. ref. 10). When we used a published procedure [11], involving addition of PCl_3 to a solution of TsiLi in THF at $0°C$, the orange solid obtained gave two ^{31}P NMR signals of almost equal height, at 234 and 600 ppm; the first of these signals arises from $TsiPCl_2$, and the other from the diphosphene TsiP=PTsi [2,4]. We were able to isolate the diphosphene in 50% yield, so the reaction of TsiLi with $TsiPCl_2$ probably provides the simplest route to this compound. Its formation under these conditions is not surprising, since it is known to be formed by treatment of I with TsiLi in THF at $-78°C$ [2].

The dichloride $TpsiPCl_2$ (II) was made analogously by addition of TpsiLi [12] in THF to PCl_3 in Et_2O. Compound II was found to be more stable in the air than I, and was kept unchanged for several months at room temperature without special protection. In a brief thermogravimetric study, weight loss began at ca. $115°C$, and 33% of the weight (corresponding to loss of one molecule of $Me_2PhSiCl$) was then lost fairly quickly by ca. $145°C$; there was then an almost level portion of the curve at ca. $145–155°C$, followed by a further fairly steep portion before a further almost level portion at ca. $170–200°C$ (the weight loss then being ca. 45%), and finally a fairly steep fall. The presence of a fairly level portion after loss of one molecule of $Me_2PhSiCl$ in the case of II and the absence of a level portion in the case of I can be attributed to the lower volatility of the initial phosphorus-containing product from II compared with that from I.

The presence of the PCl_2 group in I and II was shown by resolution-enhanced ^{31}P NMR spectra: for each compound there were two peaks separated by 0.03 ppm, with intensities in the ratio 6/4, corresponding to molecules with [35]Cl [35]Cl and [37]Cl [35]Cl which have relative abundances of 0.56/0.37.

The identity of II was confirmed by an X-ray study. As far as we are aware, this is the first on an alkylphosphonous dichloride, $RPCl_2$, though the structures of compounds with R = Me [13], Et [14], and i-Pr [15], have been determined by electron diffraction. The structure of the molecule of II is shown in Fig. 1, and a projection down the P–C bond in Fig. 2. Bond lengths and angles are given in Table

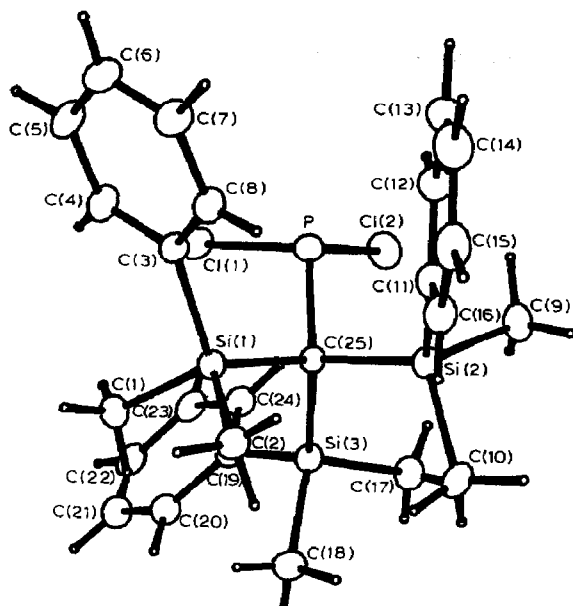Fig. 1. The molecular structure of $(Me_2PhSi)_3CPCl_2$ (II) showing atom numbering scheme.

1. As in other compounds with the Tpsi group bound to non-metallic elements [16], the mean Si–C bond lengths (1.964(3) Å) are longer than the Si–Me (1.865(4)) or Si–Ph bond lengths (1.895(4) Å), and the Si–C–Si angles (mean 109.9(6)°) are significantly larger than the Me–Si–Me (106.1(4)°) or Me–Si–Ph (105.6(11)°) angles.

The P–Cl bond lengths (mean 2.087(9) Å) are significantly longer than those in PCl_3 (2.039(1) [17] or $MePCl_2$ (2.061(3) Å). The Cl–P–Cl angle (96.1(1)°) is
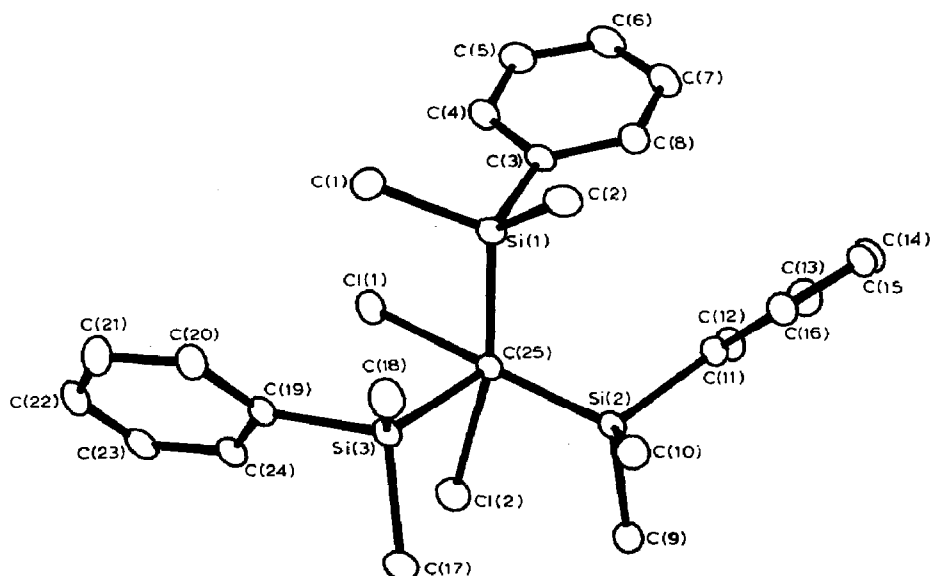

Fig. 2. The structure of II viewed along the P–C(25) bond.

Table 1

Intramolecular distances (Å) and angles (°) in $(Me_2PhSi)_3CPCl_2$ with estimated standard deviations in parentheses

(a) Bonds

Cl(1)–P	2.078(1)	Cl(2)–P	2.096(1)
P–C(25)	1.820(3)	Si(1)–C(25)	1.967(3)
Si(1)–C(1)	1.868(4)	Si(1)–C(2)	1.864(4)
Si(1)–C(3)	1.897(4)	Si(2)–C(25)	1.972(3)
Si(2)–C(9)	1.866(4)	Si(2)–C(10)	1.858(4)
Si(2)–C(11)	1.892(4)	Si(3)–C(25)	1.954(3)
Si(3)–C(17)	1.870(4)	Si(3)–C(18)	1.866(4)
Si(3)–C(19)	1.895(4)	C(3)–C(4)	1.388(5)
C(3)–C(8)	1.401(5)	C(4)–C(5)	1.395(6)
C(5)–C(6)	1.381(6)	C(6)–C(7)	1.354(6)
C(7)–C(8)	1.393(6)	C(11)–C(12)	1.387(5)
C(11)–C(16)	1.393(5)	C(12)–C(13)	1.398(6)
C(13)–C(14)	1.368(6)	C(14)–C(15)	1.357(7)
C(15)–C(16)	1.409(6)	C(19)–C(20)	1.388(5)
C(19)–C(24)	1.397(5)	C(20)–C(21)	1.393(6)
C(21)–C(22)	1.365(6)	C(22)–C(23)	1.360(6)
C(23)–C(24)	1.388(5)		

(b) Angles

Cl(1)–P–Cl(2)	96.14(6)	Cl(1)–P–C(25)	104.9(1)
Cl(2)–P–C(25)	106.0(1)	C(25)–Si(1)–C(1)	111.6(2)
C(25)–Si(1)–C(2)	111.6(2)	C(25)–Si(1)–C(3)	114.8(1)
C(1)–Si(1)–C(2)	106.5(2)	C(1)–Si(1)–C(3)	104.9(2)
C(2)–Si(1)–C(3)	106.8(2)	C(25)–Si(2)–C(9)	112.9(2)
C(25)–Si(2)–C(10)	112.5(2)	C(25)–Si(2)–C(11)	133.1(2)
C(9)–Si(2)–C(10)	106.3(2)	C(9)–Si(2)–C(11)	104.2(2)
C(10)–Si(2)–C(11)	107.1(2)	C(25)–Si(3)–C(17)	112.8(2)
C(25)–Si(3)–C(18)	109.6(2)	C(25)–Si(3)–C(19)	117.3(2)
C(17)–Si(3)–C(18)	105.6(2)	C(17)–Si(3)–C(19)	104.5(2)
C(18)–Si(3)–C(19)	106.2(2)	P–C(25)–Si(1)	103.4(2)
P–C(25)–Si(2)	103.2(2)	P–C(25)–Si(3)	120.2(2)
Si(1)–C(25)–Si(2)	110.3(2)	Si(1)–C(25)–Si(3)	110.3(2)
Si(2)–C(25)–Si(3)	109.1(2)	Si(1)–C(3)–C(4)	121.3(3)
Si(1)–C(3)–C(8)	121.8(3)	C(4)–C(3)–C(8)	116.4(3)
C(3)–C(4)–C(5)	121.9(4)	C(4)–C(5)–C(6)	119.8(4)
C(5)–C(6)–C(7)	119.8(4)	C(6)–C(7)–C(8)	120.6(4)
C(3)–C(8)–C(7)	121.5(4)	Si92)–C(11)–C(12)	120.7(3)
Si(2)–C(11)–C(16)	122.2(3)	C(12)–C(11)–C(16)	116.9(3)
C(11)–C(12)–C(13)	121.7(4)	C(12)–C(13)–C(14)	119.7(4)
C(13)–C(14)–C(15)	120.8(4)	C(14)–C(15)–C(16)	119.5(4)
C(11)–C(16)–C(15)	121.5(4)	Si(3)–C(19)–C(20)	120.7(3)
Si(3)–C(19)–C(24)	122.3(3)	C(20)–C(19)–C(24)	116.4(3)
C(19)–C(20)–C(21)	121.9(4)	C(20)–C(21)–C(22)	119.9(4)
C(21)–C(22)–C(23)	120.0(4)	C(22)–C(23)–C(24)	120.5(4)
C(19)–C(24)–C(23)	121.4(3)		

significantly smaller than that in PCl_3 (100.3(1)° or $MePCl_2$ (100.7(5)°). Figure 2 shows that the groups around the central P–C bond are neatly staggered, in contrast to those in $TsiPH_2$ [18] in which the PH_2 and $(Me_3Si)_3C$ groups are eclipsed. The angles at C(25) are however greatly distorted from the tetrahedral value: the

Si–C–P angle corresponding to the Me_2PhSi group between the two Cl atoms is 120° whereas the other two are only 103°. The crowding within the molecule is also shown by the distortion of the Tpsi group from three-fold symmetry: thus the angles between the planes of the phenyl groups and the Si_3 plane are 43, 66, and 93°, compared with 75–85° in compounds TpsiX in which X is H or a boron-containing group [19].

When a solution of TsiLi in THF was added to one of PBr_3 in Et_2O, the product after work-up appeared from its ^1H NMR spectrum to contain two species. These were separated and found to be TsiBr (apparently formed by Li/Br interchange), isolated in 36% yield, and $TsiPBr_2$, isolated in only 12% yield. The dibromide $TsiPBr_2$ was, however, obtained in good yield by treatment of I with BBr_3 in CCl_4, removal of the volatile BCl_3 probably helping to drive the reaction (eq. 1) to

$$3TsiPCl_2 + 2BBr_3 \rightarrow 3TsiPBr_2 + 2BCl_3 \tag{1}$$

completion. However, treatment of II, with BBr_3 gave a mixture of products, which were not separated. Reaction of PPh_2Cl with TsiLi gave $TsiPPh_2$ [9], but only TpsiH was isolated after work-up from the corresponding reaction with TpsiLi; TpsiLi is known to be less reactive than TsiLi towards electrophiles (e.g., Me_3SiCl [12]). Reaction of TpsiLi with $PPhCl_2$ gave TpsiCl in 36% yield, and TsiCl was the only product isolated from the reaction of TsiLi with $POCl_3$. Again, the chloride TsiCl or TpsiCl appeared to be formed by Li/Cl exchange.

The spectroscopic properties of the compounds TsiX and TpsiX (X = Cl or Br) isolated in the above reactions were compared with those of authentic samples obtained in ca. 50% yield by the reactions between TsiLi or TpsiLi and the halides CCl_4 or CBr_4. NMR data are collected in Table 2. The compound TpsiBr has apparently not been described previously.

Reaction of TsiLi with $P(OMe)_3$ in THF/Et_2O gave not $TsiP(OMe)_2$, but TsiMe, isolated in 63% yield. (The ^{31}P NMR spectrum of the solution obtained from a similar reaction with $P(OEt)_3$ indicated that $TsiP(OEt)_2$ was probably formed, but it was not isolated.) Grignard or organolithium reagents usually react with phosphites with displacement of alkoxy groups and formation of C–P bonds. Attack by the carbanion from the organometallic compound on the carbon atom of the ester is unusual, but it has been observed in reactions of sterically hindered organolithiums, e.g. Ph_3CLi, on phosphate esters $(RO)_3PO$, which give good yields of Ph_3CR [20].

The compound $TsiP(OMe)_2$ was obtained as an oil (and thus possibly somewhat impure) by treatment of I with NaOMe in MeOH; it was air-sensitive, and when

Table 2

NMR data for TsiX and TpsiX (ppm in $CDCl_3$) (Tsi = $(Me_3Si)_3C$; Tpsi = $(Me_2PhSi)_3C$; X = Cl or Br)

		TsiCl	TsiBr	TpsiCl	TpsiBr
$\delta(^1H)$	Me	0.18	0.27	0.13	0.13
	Ph	–	–	7.3–7.8	7.3–7.8
$\delta(^{13}C)$	Me	1.3	1.2	−1.0	−0.1
	C	37.9	34.3	40.1	33.5
	Ph	–	–	127.6, 129.3	127.5, 129.3
				135.2, 139.2	135.2, 139.3
$\delta(^{29}Si)$		4.8	4.8	−3.3	−2.9

heated with MeOH alone underwent protodesilylation to give $(Me_3Si)_2CHP(OMe)_2$ (also as an oil). This process presumably involved initial protonation at phosphorus, as in the corresponding reaction of $TsiPPh_2$ [9], and so was inhibited by base. (In an initial attempt to make $TsiP(OMe)_2$ from I by use of MeOH containing an inadequate amount of NaOMe only $(Me_3Si)_2CHP(OMe)_2$ was obtained *.)

With $AgNO_3$ in Et_2O, $TsiPCl_2$ was oxidised to $TsiP(O)Cl_2$ in high yield (eq. 2); the product underwent some decomposition when stored as a solid at room

$$TsiPCl_2 + AgNO_3 \rightarrow TsiP(O)Cl_2 \qquad (2)$$

temperature, but in pentane solution it was unchanged on storage for weeks at low temperature. The compound has been reported previously to be formed by hydrolysis of $TsiPCl_4$, made by treatment of I with Cl_2, but the material obtained in that way gave a ^{31}P NMR signal at 28 ppm [3], whereas for our product the signal was at 48 ppm. An attempt to make $TpsiP(O)Cl_2$ by treatment of II with $AgNO_3$ in CH_2Cl_2 led to a mixture of products which gave ^{31}P NMR signals at 49, 41, and 30 ppm. The signal at 49 ppm probably arises from $TpsiP(O)Cl_2$, and that at 30 ppm may be from the analogue of the species giving a signal at 28 ppm and thought by Escudié et al. to be $TsiP(O)Cl_2$ [3]. We hope to explore the possibility that $AgNO_3$ may be a convenient reagent for the oxidation of other of alkylphosphonous to alkylphosphonic halides. This reaction is notoriously difficult to achieve cleanly: other oxidising agents that have been used with varying degrees of success include O_3, NO_2 [21], SO_2Cl_2 [22], and sodium perchlorate in acetonitrile [23].

The phosphonic dichloride $TsiP(O)Cl_2$ was found to react very readily with MeOH to give a complex mixture of products, as indicated by ^1H and ^{31}P NMR spectroscopy. When the reaction was carried out in the presence of pyridine at $55°C$ the isolated product was the mono-desilylated species $(Me_3Si)_2CHP(O)$-$(OMe)_2$.

Reaction of I with $LiAlH_4$ is known to give $TsiPH_2$ [11], and we obtained $TpsiPH_2$ analogously from II. The compound remained unchanged when stored at room temperature without any special protection from the air.

We found that I was also reduced by $NaBH_4$ in THF, but the product, isolated as a solid, was the adduct $TsiPH_2 \cdot BH_3$. (A similar species, $PhPPH_2 \cdot BH_3$, was obtained by Wiberg and Nöth on treatment of $PhPCl_2$ with $LiBH_4$ in Et_2O at $0°C$ [24].) Addition of MeOH to a solution of the adduct in Et_2O caused evolution of gas (presumably H_2) and liberation of $TsiPH_2$. The latter was also apparently liberated on addition of pyridine to a solution of the adduct in pentane. It is of interest that the coupling constant $^1J(^{11}B-^{31}P)$ has a value of 24.0 Hz, compared with values of 27 for $PH_3 \cdot BH_3$, 35.0 for $PhPH_2 \cdot BH_3$, and 43.5 Hz for $MePH_2 \cdot BH_3$ [25]. The value of the coupling constant for BH_3 adducts of a wide range of phosphines has been observed to fall with decreasing basicity of the phosphine, and on this basis $TsiPH_2$ would appear to be less basic even than PH_3. The low value of the constant for $TsiPH_2 \cdot BH_3$ is probably, in fact, due to the bulk of the Tsi group, which distorts the geometry, and perhaps causes lengthening of the P-B bond.

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* Although I can be satisfactorily recrystallized from MeOH with little loss, it does slowly react with MeOH, to give a complex mixture of products, even at room temperature.

Experimental

General

All reactions involving chlorosilanes, lithium, organolithium reagents, and phosphorus compounds were carried out under dry nitrogen. Solvents were dried by standard procedures. TsiLi and TpsiLi were prepared as described previously [26,27].

Spectra

The ^{1}H NMR spectra were recorded (with solutions in CCl_4 unless otherwise stated) at 90 MHz, ^{31}P spectra at 32.44 MHz (with 85% H_3PO_4 as external reference), ^{11}B spectra at 25.7 MHz (with external $BF_3 \cdot OEt_2$ as reference), and ^{19}F spectra at 75.4 MHz (with external $CFCl_3$ as reference).

Mass spectra were obtained by electron impact (unless otherwise stated) at 70 eV. For halogen-containing ions the m/z values refer to the ^{35}Cl and ^{79}Br isotopes; the isotope patterns were as expected.

Preparation of TsiPCl$_2$ (I) [10]

(a) A solution of TsiLi (7.4 mmol) in a mixture of THF (40 cm^3) and Et$_2$O (10 cm^3) was added dropwise to a solution of PCl$_3$ (10.0 mmol) in Et$_2$O (ca. 20 cm^3) at room temperature (ca. 20°C) and the mixture was then stirred for 2 h. The solvent was removed under reduced pressure and the residue was extracted with boiling pentane. Cooling of the extract gave a solid, which was recrystallized quickly from boiling methanol to give TsiPCl$_2$ (1.90 g, 65%), m.p. 167°C (decomp.) (Found: C, 36.1; H, 8.2; Cl, 20.8. C$_{10}$H$_{27}$Cl$_2$PSi$_3$ calc.: C, 36.1; H, 8.1; Cl, 21.1%); ν(P–Cl)(KBr disc) 450–470, ν(P–C) 670 cm^{-1}; δ(H)(C$_6$H$_6$) 0.64 (d, ^4J(PH) 1Hz); δ(^{31}P) 233 ppm; δ(^{13}C) 3.8 (d, ^3J(PC) 6 Hz, SiMe$_3$) and 21.2 (d, ^1J(PC) 104 Hz, (Me$_3$Si)C); UV(pentane) λ_{max} 251 nm, ϵ_{max} 1800 dm^3 cm^{-1} mol^{-1}.

(b) Phosphorus trichloride (1.08 cm^3, 1.70 g, 12.4 mmol) was added dropwise during 15 min to a solution of TsiLi (50 mmol) in THF (30 cm^3) at 0°C. The mixture became orange. It was stirred at 0°C for a further 1 h, then the solvent was removed on a rotary evaporator. The deep-orange residue was extracted with pentane (50 cm^3) and the extract was filtered then evaporated. The solid residue was dissolved in CH$_2$Cl$_2$, and the solution was diluted with ca. 8 volumes of MeOH. The orange solid which separated was judged to be TsiP=PTsi (1.60 g, 50%) (Found: C, 45.5; H, 10.1. C$_{20}$H$_{54}$P$_2$Si$_6$ calcd.: C, 45.8; H, 10.3%); δ(H) (CCl$_4$) 0.30 (s); δ(P) (pentane) 600 (s) lit. [2] 600 ppm.

Preparation of TpsiPCl$_2$ (II)

A solution of TpsiLi (9.56 mmol) in THF (20 cm^3) was added dropwise during 0.5 h to a stirred solution of PCl$_3$ (1.64 g, 11.9 mmol) in Et$_2$O (25 cm^3) at room temperature. The mixture was stirred for a further 1 h, and the solvents were then removed. The residue was extracted with CH$_2$Cl$_2$ (40 cm^3), the extract was filtered then evaporated, and the residue was recrystallized from MeOH (50 cm^3) to give white crystals of TpsiPCl$_2$ (II) (3.13 g, 61%), m.p. 110°C (Found: C, 58.0; H, 6.4. C$_{25}$H$_{33}$Cl$_2$PSi$_3$ calcd.: C, 57.8; H, 6.4%); δ(H) 0.79 (18H, d, ^4J(^{1}H–^{31}P) 1Hz, SiMe$_2$) and 7.06–7.41 (15H, Ph); δ(C) (CDCl$_3$) 3.78 ppm (^3J(^{13}C–^{31}P) 5.8 Hz, SiMe$_2$), 127.1 (C(3) of Ph), 129.1 (C(4)), 136.3, (d, ^3J(^{13}C–^{31}P) 4.4 Hz, C(1)), and

137.7 (C(2)); δ(P) (C_6H_6), 228 ppm; m/z (+ve CI; NH_3) 518 (40%, $[M]^+$), 374 (100).

Reaction of TsiLi with PBr_3

A solution of TsiLi (50 mmol) in THF (30 cm^3) was added dropwise during 0.5 h to a stirred solution of PBr_3 (15.0 g, 55 mmol) in Et_2O (50 cm^3) at room temperature. The mixture was stirred for a further 1 h and the solvent then removed. The residue was shaken with pentane (60 cm^3) and the mixture then allowed to settle. The clear pentane layer was removed with a syringe and evaporated, and the residue, which appeared from its NMR spectra to be a mixture of two products, was recrystallized rapidly from cold MeOH then subjected to sublimation. A volatile component sublimed out (at 80°C at 1 mmHg) and was shown to be TsiBr (5.6 g, 36%) m.p. 191°C lit. [28] 194–195°C (Found: C, 38.4; H, 8.7%. $C_{10}H_{27}BrSi_3$ calcd.: C, 38.6; H, 8.7%); m/z 295 (20%, $[M - Me]^+$), 222 (30, $[M - SiMe_4]^+$), 201 (5, $[M - Me - MeBr]^+$ 158 (20, $[M - Me_3SiBr]^+$), 143 (60, $[M - Me - Me_3SiBr]^+$), 85 (75), 73 (100), 59 (75), and 45 (65).

The residue from the sublimation was shown to be $TsiPBr_2$ (2.5 g, 12%), m.p. 175°C (decomp.) (Found: 28.0; H, 6.4. $C_{10}H_{27}Br_2PSi_3$ calcd.: C, 28.4; H, 6.4%); δ(H) 0.66 (d, $^4J(^1H-^{31}P)$ 1 Hz, $SiMe_3$); δ(C) ($CDCl_3$) 4.25 (d, $^3J(^{13}C-^{31}P)$ 5.8 Hz); δ(P) (C_6H_6) 236 ppm; m/z 268 (10%, $[M - Me_3SiBr]^+$), 253 (65, $[M - Me_3SiBr - Me]^+$), 189 (20), 174 (20), 159 (10), 137 (70, $[SiMe_2Br]^+$), 116 (40, $[Me_3SiC\equiv P]^+$), 101, (80, $[Me_2SiC\equiv P]^+$), 73 (100), 59 (50), and 45 (70).

Reaction of TsiLi with $POCl_3$

A solution of TsiLi (25 mmol) in THF (20 cm^3) was added dropwise to a stirred solution of $POCl_3$ (4.22 g, 27.5 mmol) in Et_2O (30 cm^3) at room temperature. The mixture was stirred for a further 1 h and the solvent then removed. The residue was extracted with pentane, the extract was filtered and evaporated, and the residual solid was recrystallized from MeOH. Its ^1H NMR spectrum and analysis by GLC-MS indicated that it was a 1/2 mixture of TsiH and TsiCl. Three recrystallizations from MeOH gave TsiCl (1.66 g, 25%), m.p. 139°C (lit. [29] 139–141°C) (Found: C, 45.1; H, 10.3. $C_{10}H_{27}ClSi_3$ calcd.: C, 44.9; H, 10.1%); m/z 251 (10%, $[M - Me]^+$), 178 (20, $[M - SiMe_4]^+$), 158 (10, $[M - Me_3SiCl]^+$), 143 (45 $[M - Me - Me_3Si]^+$), 73 (100), 59 (15), and 45 (10).

Reaction of TpsiLi with $PPhCl_2$

A solution of TpsiLi (9.6 mmol) in THF (20 cm^3) was added dropwise to a stirred solution of $PPhCl_2$ (1.82 g, 10.2 mmol) in Et_2O (30 cm^3) at room temperature. The mixture was stirred for 1 h and the solvent then removed. The residue was extracted with CH_2Cl_2 (50 cm^3), and the extract filtered and evaporated. The residue was recrystallized rapidly from cold MeOH, to give TpsiCl (1.55 g, 36%), m.p. 204°C (lit: [30] 201°C) (Found: C, 66.5; H, 7.1. $C_{25}H_{33}ClSi_3$ calcd.: C, 66.4; H, 7.3%); m/z 417 (5%, $[M - Cl]^+$), 402 (10, $[M - Cl - Me]^+$), 401 (35, $[M - HCl - Me]^+$), 325 (55, $[M - PhCl - Me]^+$), 309 (10), 282 (10), 267 (20), 240 (20), 197 (20), 135 (100), and 73 (10); m/z +ve CI (NH_3) 417 (35%), 401 (20), 135 (100).

Reaction of TpsiLi with PPh_2Cl

A procedure identical with that described immediately above, but with PPh_2Cl in place of $PPhCl_2$ gave TpsiH (55%) as the only isolated product.

Reaction of TsiLi with P(OMe)₃

A solution of TsiLi (25 mmol) in THF (25 cm³) was added dropwise during 0.5 h to a stirred solution of $P(OMe)_3$ (3.4 g, 27.5 mmol) in Et_2O (30 cm³) at room temperature. The mixture was stirred overnight and the solvent then removed. The residue was extracted with CH_2Cl_2 (50 cm³), and the extract filtered then evaporated. The residue was recrystallized from MeOH to give TsiMe (3.87, 63%), m.p. 152°C (lit. [29], 155–157°C) (Found: C, 53.4.; H, 12.0. $C_{11}H_{30}Si_3$ calcd.: C, 53.7; H, 12.2%); δ(H) (CH_2Cl_2) 0.07 (27H, s, $SiMe_3$) and 1.08 (3H, s, Me); δ(C) ($CDCl_3$) 0.91 ($SiMe_3$) and 13.7 ppm (Me); m/z 246 (15% $[M]^+$) 231 (60, $[M-Me]^+$), 158 (40, $[M-SiMe_4]^+$), 143 (40, $[M-SiMe_4-Me]^+$), 131 (35), 73 (100), 59 (10), and 45 (5).

Preparation of TpsiPH₂

A solution of II (2.30 g, 5.0 mmol) in THF (20 cm³) was added dropwise to a well-stirred suspension of $LiAlH_4$ (0.10 g, 2.75 mmol) in THF (30 cm³) at room temperature. The mixture was heated under reflux for 3 h then allowed to cool, and the solvent was evaporated off under reduced pressure. The residue was extracted with CH_2Cl_2, and the extract was filtered then evaporated to leave a white solid, $TpsiPH_2$ (1.90 g, 95%), m.p. 91°C (Found: C, 66.3; H, 7.6. $C_{25}H_{35}PSi_3$ calcd.: C, 66.7; H, 7.3%); δ(H) (CCl_4) 0.21 (18H, s, $SiMe_2$) 3.35 (2H, d, $^1J(^1H-^{31}P)$ 193 Hz, PH_2), and 7.07–7.47 (15H, m, Ph); δ(C) ($CDCl_3/CH_2Cl_2$) -0.20 (d, $^3J(^{13}C-^{31}P)$ 5.9 Hz, $SiMe_2$), 127.1 (C(3) of Ph), 128.8 (C(4)), 135.3 (s, C(2)); δ(P) -137 ppm (t); m/z (+ve CI; NH_3) 451 (60%, $[M+H]^+$), 450 (20, $[M]^+$), 73 (100).

Preparation of TsiPH₂ · BH₃

A solution of I (1.00 g, 3.00 mmol) in THF (15 cm³) was added dropwise to well-stirred suspension of $NaBH_4$ (0.15 g, 3.9 mmol) in THF (20 cm³) at room temperature. The mixture was heated under reflux for 3 h then allowed to cool, and the solvent was removed under reduced pressure. The residue was extracted with pentane, and the extract was evaporated to leave $TsiPH_2 \cdot BH_3$ (0.82 g, 96%), m.p. 108°C (Found: C, 43.9; H, 11.4. $C_{10}H_{32}BPSi_3$ calcd.: C, 43.2; H 11.5%); δ(H) (CCl_4) 0.31 ($SiMe_3$); δ(P) (pentane) -46 ppm (br); δ(B) (pentane) -36.5 ppm ($^1J(^{11}B-^{31}P)$ 24.0 Hz, $^1J(^1H-^{11}B)$ 104 Hz); m/z 264 (50%, $[M-BH_3]^+$), 249 (35, $[M-BH_3-Me]^+$), 73 (100).

Preparation of TsiP(O)Cl₂

A solution of I (1.00 g, 3.0 mmol) in Et_2O (50 cm³) was added to solid $AgNO_3$ (0.63 g, 3.7 mmol). The mixture was stirred at room temperature with protection from the light, and small samples were removed from time to time for determination of the ^1H NMR spectrum. This showed formation of a single product, and when all the starting material had disappeared (48 h) the solvent was removed and the residue was extracted with pentane. The extract was filtered through pentane-washed charcoal and then evaporated to leave $TsiP(O)Cl_2$ (1.0 g, 95%), m.p. 112°C (Found: C, 34.3; H, 7.9. $C_{10}H_{27}Cl_2OPSi_3$ calcd.: C, 34.4. H, 7.7%); δ(H) 0.67; δ(P) (C_6H_6) 48 ppm; m/z 348 (35%, $[M]^+$), 333 (70, $[M-Me]^+$), 313 (10, $[M-Cl]^+$), 73 (100).

Reaction of II with AgNO₃

A solution of II (0.50 g, 0.96 mmol) in CH_2Cl_2 was added to solid $AgNO_3$ (0.24 g, 1.44 mmol), and the mixture was stirred at room temperature with protection

from the light. Samples removed for ^{31}P NMR spectroscopy gave three peaks, at 49, 41, and 30 ppm, in addition to that from the starting material. When the starting material had been consumed the solution was filtered through charcoal (pre-washed with CH_2Cl_2) and evaporated to leave a thick oil, which gave the same three ^{31}P NMR signals, and was probably a mixture of three phosphorus-containing products.

Preparation of TsiPBr₂

Preparation of TsiPBr$_2$

A solution of I (0.50 g, 1.25 mmol) in CCl_4 (20 cm^3) was treated dropwise with a (1 M) solution of BBr_3 (1.00 mmol) in CH_2Cl_2 (1 cm^3) at room temperature. The mixture was stirred overnight, then volatile materials were removed. The residue was washed rapidly with cold MeOH, dried under vacuum, and shown to be TsiPBr$_2$ (0.54 g, 85%), m.p. 175 °C. (decomp.) (Found: C, 28.35; H, 6.4. $C_{10}H_{27}Br_2PSi_3$ calc.: C, 28.4; H, 6.4%) with NMR and mass spectra effectively identical to those described above.

Reaction of TsiPCl$_2$ with NaOMe / MeOH

A solution (0.50 M) of NaOMe (3.00 mmol) in MeOH (6.00 cm^3) was added dropwise to solid I (0.50 g, 1.5 mmol) with stirring at 0 °C. The mixture was stirred for an additional 0.5 h and the solvent then removed under reduced pressure. The residue was extracted with CH_2Cl_2 (20 cm^3), and the extract was filtered then evaporated under reduced pressure to leave a viscous oil, which was probably TsiP(OMe)$_2$ (0.46 g, 95%); δ(H) (C_6H_6) 0.47 (27 H, s, SiMe$_3$) and 3.56 (6H, d, $^3J(^1H-^{31}P)$ 12 Hz, OMe); δ(P)(CH_2Cl_2) 211 p.p.m. (septet, $^3J(^1H-^{31}P)$ 12 Hz); m/z 324 (10%, $[M]^+$), 309 (10, $[M - Me]^+$), 73 (100).

Reaction of TsiP(OMe)$_2$ with MeOH

A mixture of TsiP(OMe)$_2$ (0.46 g, 1.24 mmol) and MeOH (0.10 cm^3) was kept at 70 °C for 10 min. Volatile material was then removed under reduced pressure to leave a colourless viscous oil, which was judged to be (Me$_3$Si)$_2$CHP(OMe)$_2$ (0.34 g, 97%); δ(H) (C_6H_6) 0.44 (18H, d, $^4J(^1H-^{31}P)$ 1 Hz, SiMe$_3$) and 3.56 (6H, d, $^3J(^1H-^{31}P)$ 12 Hz, OMe); δ(P) (C_6H_6) 211 ppm (d of septets, $^2J(^1H-^{31}P)$ 25 Hz, $^3J(^1H-^{31}P)$ 12 Hz; m/z 252 (20%, $[M]^+$), 237 (15, $[M - Me]^+$), 89 (100), 73(90).

Reaction of TsiP(O)Cl$_2$ with MeOH

A solution of pyridine (0.24 g, 3.0 mmol) in MeOH (10 cm^3) was added dropwise with stirring to TsiP(O)Cl$_2$ (0.50 g, 1.43 mmol) at 55 °C. The mixture was stirred for a further 3 h at 55 °C and the solvent then removed to leave a colourless oil, which was judged to be (Me$_3$Si)$_2$CHPO(OMe)$_2$ (0.37 g, 97%); δ (H) (C_6H_6) 0.45 (18H, s, SiMe$_3$) and 3.5 (6H, d, $^3J(^1H-^{31}P)$ (12 Hz, OMe); δ(P) (pentane) 38 ppm (d of septets, $^3J(^1H-^{31}P)$ 25 Hz, $^3J(^1H-^{31}P)$ 12 Hz); m/z 268 (30, $[M]^+$), 253 (95, $[M - Me]^+$), 133 (100), 73 (90).

Reaction of II with sodium naphthalene

A solution of II (1.0 g, 1.92 mmol) in THF (20 cm^3) was added dropwise during 0.5 h to a solution of sodium naphthalene (5.0 mmol) in THF (20 cm^3) at -78 °C. The mixture was stirred at -78 °C for a further 1 h and the ^{31}P spectrum of the solution was then recorded. This showed two singlets, one at 228 ppm attributable to II, and the other at 603 ppm; the latter suggested the formation of a P=P bond. Attempts to isolate the product were unsuccessful.

Preparation of TpsiBr

A solution of TpsiLi (5.0 mmol) in THF (50 cm^3) was added dropwise during 20 min to CBr$_4$ (1.99 g, 6.0 mmol) in diethyl ether (10 cm^3) at 0°C. The solution became brown. It was allowed to warm to 25°C during 3 h, the solvent was then evaporated, and the residue was extracted into diethyl ether (3 × 40 cm^3). The extract was filtered, concentrated, and cooled, and the yellowish crystals were separated, and recrystallised from methanol to give white needles of TpsiBr. Yield 1.25 g, 50% m.p. 213°C (sealed capillary) (Found: C, 60.1; H, 6.7; C$_{25}$H$_{33}$BrSi$_3$ calc.: C, 60.3; H, 6.7%) m/z (+ve CI NH$_3$ 514 (100%, [M + NH$_4$]$^+$) 419 (5, [M − Ph]$^+$), 346 (15, [M − SiMe$_3$Ph]$^+$), 301 (10), 284 (20 [M − SiPhMe$_2$]$^+$), 152 (25), and 135(30).

TpsiCl, TsiCl and TsiBr were made similarly. For TsiBr it was necessary to take care that all the methyllithium used in the preparation of TsiLi had disappeared before addition of CBr$_4$ in order to prevent contamination of the product with TsiMe.

Table 3

Fractional atomic coordinates (× 10^4) for nonhydrogen atoms of (Me$_2$PhSi)$_3$CPCl$_2$

	x	y	z
Cl(1)	2452.4(10)	886.4(6)	6943.5(6)
Cl(2)	1008.1(10)	−666.8(7)	6362.2(7)
P	3028.6(10)	−240.5(6)	6594.0(5)
Si(1)	5315.5(10)	−86.5(6)	7853.6(6)
Si(2)	4242.6(10)	−1772.2(6)	7150.6(6)
Si(3)	2467.5(10)	−843.7(6)	8414.3(6)
C(25)	3675(3)	−719(2)	7518(2)
C(1)	4886(4)	695(2)	8593(2)
C(2)	6704(4)	−707(2)	8355(2)
C(3)	6137(3)	464(2)	7008(2)
C(4)	5883(4)	1262(2)	6875(2)
C(5)	6580(4)	1693(2)	6307(3)
C(6)	7563(4)	1324(3)	5865(2)
C(7)	7851(4)	550(3)	5989(2)
C(8)	7155(4)	117(2)	6554(2)
C(9)	2842(4)	−2290(2)	6540(3)
C(10)	4752(4)	−2444(2)	7999(2)
C(11)	5747(4)	−1737(2)	6469(2)
C(12)	5562(4)	−1461(2)	5686(2)
C(13)	6634(5)	−1480(3)	5155(2)
C(14)	7898(4)	−1784(3)	5404(3)
C(15)	8118(4)	−2080(3)	6157(3)
C(16)	7042(4)	−2053(2)	6696(2)
C(17)	1155(4)	−1647(2)	8241(2)
C(18)	3522(4)	−1138(3)	9338(2)
C(19)	1416(4)	47(2)	8705(2)
C(20)	1692(4)	425(2)	9436(2)
C(21)	834(5)	1018(3)	9709(2)
C(22)	−312(4)	1244(2)	9249(2)
C(23)	−617(4)	887(2)	8529(2)
C(24)	226(4)	291(2)	8257(2)

Crystal structure determination of II

Crystal data: $C_{25}H_{33}Cl_2PSi_3$, $M = 519.7$, monoclinic, space group $P2_1/n$, a 9.655(1), b 16.925(3), c 16.649(4) Å, β 93.10(1)° $U = 2716.6$ Å^3, $Z = 4$, D_c 1.27 g cm^{-3}, $F(000) = 1096$, Mo-K_α radiation, λ 0.71069 Å, μ 4.38 cm^{-1}.

Data were measured on an Enraf–Nonius CAD4 diffractometer with a crystal of size $0.65 \times 0.4 \times 0.3$ mm. Intensities for $h,k \pm l$ reflections with $2 < \theta < 25°$ were measured by a $\theta/2\theta$ scan with $\Delta\theta = (0.8 + 0.35 \tan \theta)°$. Two standard reflections monitored every 30 min showed no significant variation. Data were corrected for Lorentz and polarisation effects but not for absorption: 3369 unique reflections with $|F|^2 > \sigma|F^2|$ were used in the structure refinement.

The positions of P, Cl, and Si atoms were found by direct methods [31] and C and H atoms from difference maps. Full matrix least squares refinement with anisotropic temperature factors for non-hydrogen and isotropic temperature factors for hydrogen atoms converged at $R = (\Sigma||F_o| - |F_c||)/(\Sigma|F_o|) = 5.0\%$ and $R' = \{[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2} = 5.9\%$. No feature > 0.5 e Å^{-3} was observed on a final difference map.

A PDP 11/34 computer and the Enraf–Nonius Structure Determination Package were used for the structure solution and refinement. Final atom coordinates are given in Table 3. Supplementary data are availaable from the authors.

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