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# 1,2,3,4-Tetramesityl-1,4-bis(tri-*n*-butyltin)tetraphosphane: synthesis and molecular structure†

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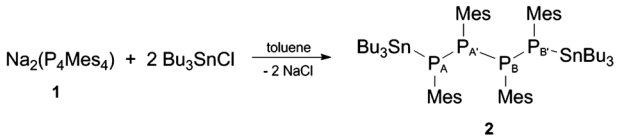
**The reaction of $[Na_2(thf)_4(P_4Mes_4)]$ (1) with tributyltin chloride gives 1,2,3,4-tetramesityl-1,4-bis(tri-*n*-butyltin)tetraphosphane (2) which is stable towards disproportionation in solution at room temperature.**

Homoatomic structures are well known for non-metals.[1] Group 15 elements are always bound to three other atoms in their homoatomic structures. These elements also have the tendency to form homoatomic rings, chains and macromolecules, which can be polyanions, polycations or neutral compounds.[2] However, most compounds with E–E bonds (E = P, As, Sb) typically undergo a continuous dynamic reorganisation, which is more pronounced for the higher homologues. Thus, it is possible to obtain short-chain linear oligophosphanes, but not the analogous oligoarsanes or stibanes.[3] While diarsanes,[4] distibanes[5] and dibismutanes[6] have been described, there are only few examples of higher linear, single-stranded oligomers. Neutral *catena*-stibanes such as tristibanes $R_2Sb–SbR'–SbR_2$ (R = Me, Et, Ph; R′ = Me, Et, *t*Bu, $CH(SiMe_3)_2$, Ph)[7] and tetrastibanes $R'_2Sb–SbR–SbR–SbR'_2$ (R = Et, R′ = Ph;[7] R = $CH_2SiMe_3$, R′ = Me, Ph)[8] have been reported, but no crystal structures thereof.

To date, only a limited number of *catena*-phosphanes with general formula $X–(P_nR_n)–X$ (with X = H, $SiMe_3$) have been reported, where *n* = 2, R = Ph, 2,4,6-$Me_3C_6H_2$ (Mes),[9] *n* = 3, R = Ph,[10] and *n* = 4, R = *t*Bu, Ph, Mes.[11] One major problem is the sensitivity of these compounds towards disproportionation, and thus only a few of them have been fully characterised and further explored. The disproportionation reactions of tetraphosphanes include rearrangements that follow a four-centre mechanism predominantly involving P–P bonds[12] and lead to shorter linear primary or secondary phosphanes as well as monocyclic phosphanes.[13]

We here report the synthesis of a stable and easier-to-handle tetraphosphane, namely 1,2,3,4-tetramesityl-1,4-bis(tri-*n*-butyltin)-tetraphosphane (**2**), which was obtained by reaction of $[Na_2(thf)_4(P_4Mes_4)]$[14] (**1**) with tributyltin chloride at −78 °C. Recrystallisation from DME gave crystals of the pure compound in 80% yield (Scheme 1).‡ Tetraphosphane **2** is stable in solution at room temperature and stable towards disproportionation reactions.




1 2

**Scheme 1** Synthesis of 1,2,3,4-tetramesityl-1,4-bis(tri-*n*-butyltin)tetraphosphane (**2**).

In the $^{31}P$ NMR spectrum of the reaction mixture, two multiplets ($\delta_P$ = −35.7 and −113.3 ppm) were observed indicating an AA′BB′ spin system (if the coupling to $^{117}Sn/^{119}Sn$ is neglected; $^1J_{PSn}$ = 863.5 Hz), which is characteristic of compound **2** (Table 1). At −80 °C, a set of four additional multiplets ($\delta_P$ = −30.5, −47.4, −114.3, −124.8 ppm) indicative of an ABCD spin system appeared besides the signals of **2** as the main product and a signal of $PHMes(SnBu_3)$[15] (Fig. 1).[16] Assuming that the inversion at the phosphorus atoms is slow on the NMR timescale, which is plausible in the case of open-chain phosphanes at low temperature, these additional multiplets could be assigned to a different configurational isomer of **2**. Considering the intensity of the signals in the reaction mixture, the concentration of this isomer is much lower than that of the main diastereomer of

**Table 1** $^{31}P\{^1H\}$ NMR parameters of $(R_P,R_P,S_P,S_P)$-$P_4Mes_4(SnBu_3)_2$ (**2**), $(R_P,S_P,R_P,S_P)$-$P_4H_2Mes_4$ and $(R_P,S_P,R_P,S_P)$-$P_4Ph_4(SiMe_3)_2$

| | **2**[a] | $(R_P,S_P,R_P,S_P)$-$P_4H_2Mes_4$ (ref. 11*f* and 18) | $(R_P,S_P,R_P,S_P)$-$P_4Ph_4(SiMe_3)_2$ (ref. 11*a*) |
|---|---|---|---|
| $\delta_A$ | −38.6 ppm | −50.4 ppm | −27.6 ppm |
| $\delta_B$ | −119.6 ppm | −104.9 ppm | −88.3 ppm |
| $^1J_{AB} = {}^1J_{A'B'}$ | −197.7(4) Hz | −183.5 Hz | −140.31 Hz |
| $^1J_{BB'}$ | −169.2(3) Hz | −170.4 Hz | −169.7 Hz |
| $^2J_{AB'} = {}^2J_{A'B}$ | +125.5(3) Hz | +31.0 Hz | +128.1 Hz |
| $^3J_{AA'}$ | +24.6(3) Hz | +11.8 Hz | +12.8 Hz |

[a] The chemical shifts and coupling constants were calculated using the simulation program SpinWorks 3 and are in good agreement with the experimental data.[17]

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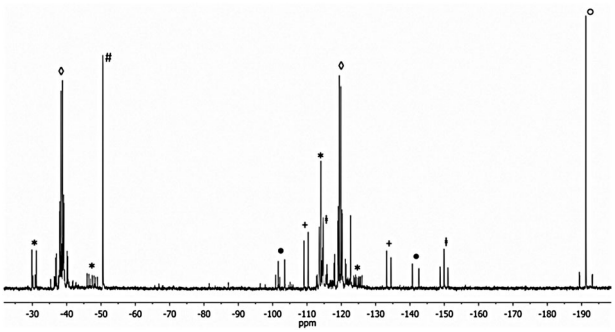

**Fig. 1** $^{31}P\{H\}$ NMR spectrum of the reaction mixture in $D_8$-THF at −80 °C (◇ = ($R_P,R_P,S_P,S_P$)-**2**, * = ABCD spin system (different diastereomer of **2**), ‡ = *cyclo*-($P_3Mes_3$), # = *cyclo*-($P_4Mes_4$), ○ = $PHMes(SnBu_3)$, + = AB spin system (not assigned), ● = AB spin system (not assigned)).

$P_4Mes_4(SnBu_3)_2$ (**2**). In addition, two sets of doublets (AB spin systems) at $\delta$ = −102.6, −141.6 ppm ($^1J_{PP}$ = 308.3 Hz) and $\delta$ = −109.7, −133.8 ppm ($^1J_{PP}$ = 198.9 Hz) indicate that the $P_4$ chain was cleaved to give two different compounds that contain an unsymmetrical $P_2$ moiety in which no coupling to tin is observed. However, these resonances could not be further assigned.

Starting with tetraphosphanes, the structural diversity of the open-chain oligophosphanes becomes quite complex. Generally, with increasing steric demand of the organic substituents on the phosphorus atoms, the configurations and conformations of the possible isomers are significantly influenced by steric factors in addition to the tendency for *gauche* orientation of neighbouring lone pairs of electrons. Theoretically, in the case of 1,2,3,4-tetramesityl-1,4-bis(tri-*n*-butyltin)tetraphosphane (**2**), there are six possible configurational isomers. However, the experimentally observed spectrum at room temperature shows that only the *erythro*,*meso*,*erythro* (or $R_P,R_P,S_P,S_P$) diastereomer is formed due to the presence of bulky mesityl substituents. In contrast to $P_4Ph_4(SiMe_3)_2$,[11a] in which the –PPh($SiMe_3$) groups are the bulkiest substituents of the two central phosphorus atoms, in **2**, there is an obvious repulsion between the bulky mesityl groups themselves, without any major effect of the $SnBu_3$ groups. Therefore, the *erythro*,*meso*,*erythro* arrangement of the $P_4$ chain is preferred (Fig. 2). The small amounts of the other observed isomer are due to the less preferred orientation of the lone pairs of electrons of the terminal P–P bonds. A helical structure of the $P_4$ chain is also feasible.

The assignment of the spin systems observed in the $^{31}P\{^1H\}$ NMR spectrum to the corresponding stereoisomer was carried out by comparison with similar compounds, as well as by considering steric and electronic effects. For example, the silylated tetraphosphane $P_4Ph_4(SiMe_3)_2$ exists as four (of six possible) different stereoisomers at low temperature, of which the ($R_P,S_P,R_P,S_P$) diastereomer is the predominant isomer. This stereoisomer corresponds to a *meso* form of the compound with a coplanar arrangement of the phenyl groups at 1,3- and 2,4-positions, respectively, and the lone pairs of electrons have an optimal *trans* orientation.[11a] Similar observations were made for $P_4H_2Mes_4$, which exists solely as a *meso* isomer, *i.e.*, the ($R_P,S_P,R_P,S_P$) diastereomer.[18] The $^{31}P\{^1H\}$ NMR parameters for ($R_P,S_P,R_P,S_P$)-$P_4Ph_4(SiMe_3)_2$ and ($R_P,S_P,R_P,S_P$)-$P_4H_2Mes_4$ and those observed for the main isomer of **2**, which was assigned as a *meso* form, in this case the ($R_P,R_P,S_P,S_P$) diastereomer, are listed in Table 1. The ($R_P,R_P,S_P,S_P$) diastereomer, in which the bulky mesityl groups are positioned in the sterically least hindered *erythro*,*meso*,*erythro* configuration, is also present in the solid state. Compound **2** crystallises in the triclinic space group $P\bar{1}$ with one formula unit in the unit cell. The $P_4$ chain resides on an inversion centre, resulting in an *anti*-periplanar arrangement (Fig. 3).

To date, only one other mesityl-substituted tetraphosphane with an *anti*-periplanar conformation, namely $P_4H_2Mes_4$, has been characterised. In contrast to the latter, the structurally characterised silylated tetraphosphane $P_4tBu_4(SiMe_3)_2$ (ref. 11*a*), exhibits a *syn*-periplanar arrangement. The P–P bond lengths of **2** [2.2178(5) and 2.2272(7) Å] are in the typical range for P–P single bonds[19] and also agree with those reported for $P_4H_2Mes_4$ (2.23 Å).[11f] The P–P bond lengths in $P_4tBu_4(SiMe_3)_2$ are slightly shorter and have an average value of 2.18 Å for the terminal P–P bonds and 2.21 Å for the internal P–P bond.[11c] The Sn–P bond length [2.5222(4) Å] is in the expected range of $Sn^{IV}$–P single bonds, *e.g.* 2.520(1) and 2.503(1) Å (R = Me)[20] or 2.545(3) and 2.536(3) Å (R = *t*Bu)[21] in the five-membered heterocycle *cyclo*-$(PtBu)_4SnR_2$, 2.513(1), 2.533(2), 2.525(1) and 2.502(1) Å in the six-membered heterocycle *cyclo*-1,4-{$Sn(CH_3)_2$($t$BuP-P$t$Bu)$_2$}.[20] $Sn^{II}$–P bonds are typically longer (*e.g.* 2.640(2)–2.699(2) Å in the heteroleptic

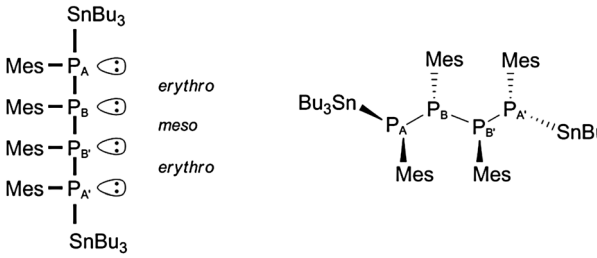


**Fig. 2** Stereochemistry of 1,2,3,4-tetramesityl-1,4-bis(tri-*n*-butyltin)tetraphosphane (**2**).

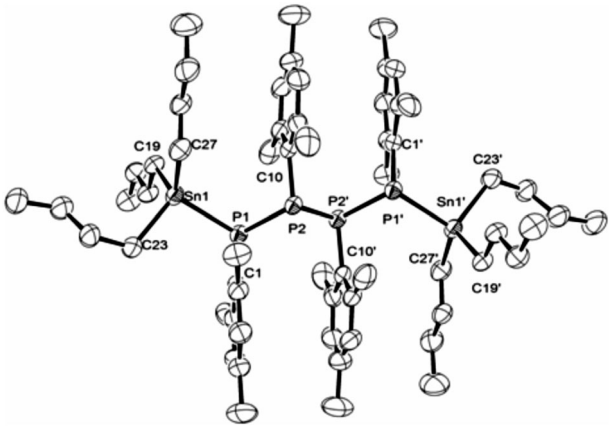


**Fig. 3** Molecular structure of 1,2,3,4-tetramesityl-1,4-bis(tri-*n*-butyltin)tetraphosphane (**2**). H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–P2 2.2178(5), P2–P2′ 2.2272(7), Sn1–P1 2.5222(4); C23–Sn1–P1 101.08(7), Sn1–P1–P2 106.28(2), C1–P1–P2 99.87(5), P1–P2–C10 107.47(5), P1–P2–P2′ 96.98(2) (ellipsoids are shown at 50% probability).

 

cage compound $[(SnCl)_4(FcP–PFc)_2]$ [Fc = $Fe(C_5H_4)(C_5H_5)$],[22] 2.599(2)–2.631(2) Å in $[\{(PhP–PPh)Sn(\mu\text{-}PPh)\}_2(Na{\cdot}PMDETA)_4]{\cdot}$toluene [PMDETA = $(Me_2NCH_2CH_2)_2NMe$] and 2.578(2)–2.884(2) Å in $[\{Sn(\mu_3\text{-}Ppy)\}_3\{Sn(\mu_3,\mu_1\text{-}pyP–Ppy)\}_3]{\cdot}2.5THF$ (py = 2-pyridyl)[23]).

Surprisingly, **2** proved to be extremely unreactive in substitution reactions (elimination of $Bu_3SnCl$) and transmetallation reactions.[24] The stability of the Sn–P bond could be due to additional interaction of the phosphorus lone pair ($p_\pi$) with the vacant d orbital of tin;[15e] however, there is no evidence for partial π bonding in **2**. In this case, the very low reactivity is most probably due to steric effects of the bulky mesityl groups.

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## Notes and references

‡ **2:** a solution of $Bu_3SnCl$ (0.15 mL, 0.55 mmol) in toluene (5 mL) was carefully added dropwise at −78 °C to an orange solution of $[Na_2(thf)_4P_4Mes_4]$[14] (0.25 g, 0.26 mmol) in toluene (50 mL). The resulting yellow solution was allowed to warm to room temperature over 2 h and then stirred for an additional 2 h. The solvent was removed under vacuum and the resulting yellow oil was extracted with $Et_2O$ (2 × 30 mL). The yellow $Et_2O$ solution was filtered and $Et_2O$ was evaporated. The remaining crystalline yellow solid was dissolved in DME (1 mL) and the solution stored at −20 °C. Yellow crystals of **2** formed within one day. Yield: 0.25 g (80%). $^1$H NMR (25 °C, 400.13 MHz, $D_8$-THF), $\delta$ = 0.8–1.0 (br m, 18H, $CH_3$ in Bu), 1.1–1.6 (br m, 36H, $CH_2$ in Bu), 1.9–2.8 (br m, 36H, $CH_3$ in Mes), 6.2–6.8 (br m, 8H, 3,5-H in Mes); $^{13}C\{^1H\}$ NMR (25 °C, 100.61 MHz, $D_8$-THF), $\delta$ = 11.8 (s, $CH_3$ in Bu), 12.7 (s, $CH_2$ in Bu), 20.0 (s, $CH_2$ in Bu), 128.3 (s, 3,5-C in Mes–$P_B$), 129.5 (s, 3,5-C in Mes–$P_A$), 136.4 (s, 4-C in Mes–$P_A$), 138.2 (s, 4-C in Mes–$P_B$), 143.5 (s, 2,6-C in Mes–$P_A$), 144.7 (m, 1-C in Mes), 146.1 (s, 2,6-C in Mes–$P_B$); $^{31}$P NMR (25 °C, 161.98 MHz, $D_8$-THF), see Table 1; $^{119}$Sn NMR (25 °C, 149.21 MHz, $D_8$-THF), $\delta$ = −5.8 (d, $^1J_{SnP}$ = 863.5 Hz); elemental analysis: found, C 58.51%, H 8.41%, calcd for $C_{60}H_{98}Sn_2P_4$, C 61.03%, H 8.37%. Crystal data for **2:** $C_{60}H_{98}Sn_2P_4$, FW = 1180.64, triclinic, space group $P\bar{1}$, $Z$ = 1, $a$ = 9.5430(2), $b$ = 13.0225(4), $c$ = 14.6643(4) Å, $\alpha$ = 110.296(2)°, $\beta$ = 99.499(2)°, $\gamma$ = 106.251(2)°, $V$ = 1569.89(7) Å$^3$, $\mu$(Mo-Kα) = 0.931 mm$^{-1}$, $\rho_{calc}$ = 1.249 Mg m$^{-3}$, $T$ = 200(2) K. Data were collected on an Agilent GEMINI CCD diffractometer. Of a total of 34 675 reflections, 9560 were unique ($R_{int}$ = 0.0205). The structure was solved by direct methods (Sir-92)[25] and refined by full-matrix least-square method on $F^2$. Final $R_1$ = 0.0349 (all data) and w$R_2$ = 0.0671 (all data). CCDC 936270 (**2**).

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