Synthesis, crystal and molecular structure of a novel organoantimony cage compound, $C_4Bu^t{}_4P_4Sb_2$

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The reaction of the hetero-ring anion $[P_2SbC_2Bu^t{}_2]^-$ with $FeCl_3$ affords the organoantimony cage compound, $C_4Bu^t{}_4P_4Sb_2$, *via* a proposed oxidative coupling reaction; the X-ray crystal structure of the cage displays weak intermolecular interactions.

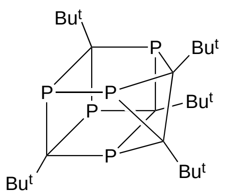
The chemistry of organophosphorus cage compounds is a rapidly expanding area that derives its current importance from the remarkable similarities such compounds show to their hydrocarbon cage counterparts.[1] Several synthetic routes to these compounds have been developed but the oxidative coupling of polyphospholyl ions is the route most relevant to the work described here.[2] For example, Nixon and coworkers have reported that the treatment of a 1 : 1 mixture of the ions $[1,2,4\text{-}P_3C_2Bu^t{}_2]^-$–$[1,3\text{-}P_2C_3Bu^t{}_3]^-$ with $FeCl_3$ leads to low yields of the cage, $P_5C_5Bu^t{}_5$ **1**, *via* an unknown mechanism.[3] The formation of organophosphorus cage compounds *via* oxidative coupling reactions can be blocked if the reacting polyphospholyl ion is sufficiently sterically protected, as is the case in the reaction of $[1,3\text{-}P_2C_3Bu^t{}_3]^-$ with $[RuCl_2(\eta^4\text{-}C_8H_{12})]_n$ which yields **2** among other products.[4] Moreover, the absence of any known uncoordinated poly-arsolyl, -stibolyl or -bismolyl anions precludes the existence of heavier group 15 element organometallic cages derived from oxidative coupling reactions. However, coupling of their monosubstituted counterparts is known to yield compounds of the type **3**, which can possess solid-state intermolecular interactions (E = Sb, Bi) that impart thermochromic properties to these species.[5]

We have recently developed a high-yielding synthetic route to the diphosphastibolyl ring anion $[P_2SbC_2Bu^t{}_2]^-$ **4**,[6] which we have incorporated into a range of organometallic complexes, *viz.* $[Ru(\eta^5\text{-}C_5R_5)(\eta^5\text{-}P_2SbC_2Bu^t{}_2)]$ (R = H, Me),[7] $[M(\eta^5\text{-}P_2SbC_2Bu^t{}_2)(\eta^4\text{-}C_8H_{12})]$ (M = Rh, Ir) and $[Co(\eta^5\text{-}P_2SbC_2Bu^t{}_2)(\eta^4\text{-}P_2SbC_2HBu^t{}_2)]$.[8] Our interests have now extended to an examination of the formation of organometallic cages *via* oxidative coupling reactions of **4**. The results of these investigations are reported herein.

Treatment of a dme solution of $FeCl_3$ with 1 equiv. of $[Li(tmeda)_2]$ **4** (Scheme 1) leads to the formation of the air- and moisture-stable cage compound, $C_4Bu^t{}_4P_4Sb_2$ **6** (mp 82 °C decomp.), in good yield (61%) after chromatographic work-up (Kieselgel, hexane). Compound **6** can also be prepared in lower yields by the reactions of $[Li(tmeda)_2]$ **4** with either $InCl_3$, $PbCl_2$ or SbF_3. It seems likely that the reaction mechanism involves an initial coupling to give the intermediate, **5**, which then undergoes a [4 + 2] cycloaddition reaction to give the final product, **6**. If this is so, it is surprising that the coupling occurs through the most sterically hindered heterocentre on one of the rings, *i.e.* the P centre adjacent to two *tert*-butyl substituted C centres. It is also surprising that only one set of enantiomers is formed despite the numerous isomers that are possible if the coupling reaction were to occur through any of the heterocentres on each ring and if there was no specificity to the possible subsequent cycloaddition reactions.

The spectroscopic data‡ for **6** support its proposed structure. Its $^{31}P\{^1H\}$ NMR spectrum is pseudo-first order and has been successfully simulated as an AMNX spin system with four inequivalent phosphorus resonances; two at low field (P_A, P_X) in the region consistent with phosphaalkenes, and two in the higher field saturated phosphorus region (P_M, P_N). The lowest field signal (δ 363.4) shows considerable broadening which suggests it arises from the low-coordinate phosphorus centre, P(1), adjacent to the quadrupolar antimony centre, Sb(1). This would necessitate the highest field signal (δ −18.6) to originate from P(2) due to its two-bond coupling (28 Hz) to P(1). The assignment of the remaining signals, P(4) (δ 356.5) and P(3) (δ 32.5) logically follows. Interestingly, there is a very large two-bond coupling (137 Hz) between P(2) and P(3). This is perhaps best explained as a through space coupling which results from the very short intramolecular P(2)–P(3) distance (*vide infra*). Both the ^1H and ^{13}C NMR spectra of **6** are as expected and highlight four inequivalent *tert*-butyl groups. The mass spectrum of **6** exhibits a molecular-ion peak with the correct isotopic distribution.

The molecular structure of **6**§ is depicted in Fig. 1. All bond lengths within the structure are normal for single bonded interactions except those for P(1)–C(2) [1.681(4) Å] and P(4)–C(12) [1.689(4) Å] which are consistent with localised



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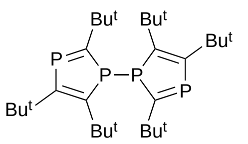

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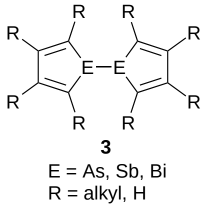
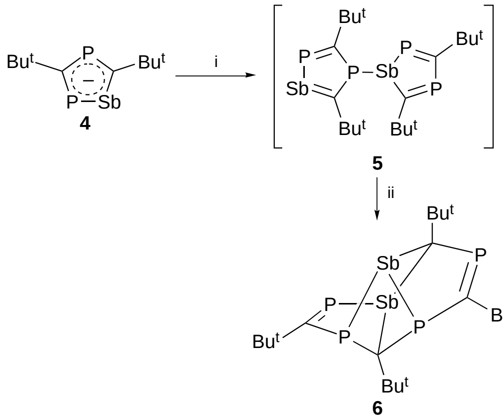


3

E = As, Sb, Bi
R = alkyl, H



Scheme 1 *Reagents and conditions*: i, $FeCl_3$, dme, 18 h, 25 °C; ii, [4 + 2] cycloaddition

P–C double bonds. Compound **6** contains the first example of a structurally characterised diphosphastibacyclobutane fragment [Sb(2)–P(3)–C(1)–P(2)] which has very short cross-ring P···P (2.822 Å) and Sb···C (3.024 Å) distances which are well within the sum of the van der Waals radii (3.8 and 4.04 Å respectively[9]) for these atom combinations. There are also two polyhetero six-membered rings within the structure [P(1)=C(2)–P(2)–Sb(2)–C(11)–Sb(1) and P(4)=C(12)–P(3)–C(1)–Sb(1)–C(11)] which are also the first examples of such heterocyclic fragments. Another feature of the structure of **6** became evident from an examination of its cell packing diagram (Fig. 2) which shows the molecules to be linked in infinite one-dimensional arrays through weak intermolecular interactions [Sb(2)···P(1) 3.621(6) Å, P(2)···P(1) 3.652(5) Å] which are less than the sum of the van der Waals radii of the atoms involved [Sb–P (4.1 Å), P–P (3.8 Å)].

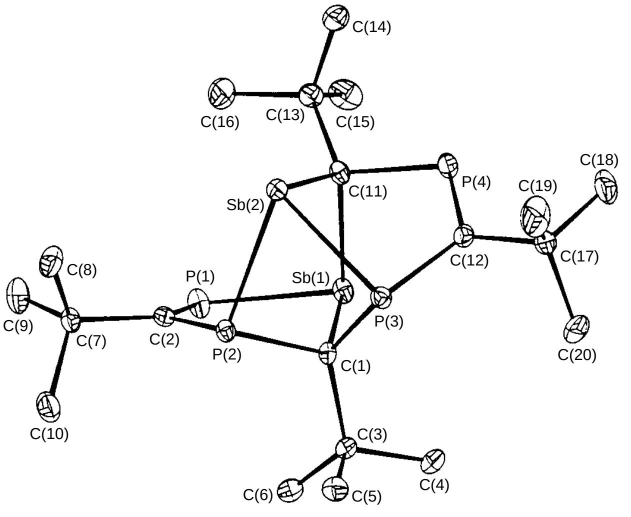


Fig. 1 Molecular structure of $C_4Bu^t{}_4P_4Sb_2$ **6**. Selected bond lengths (Å) and angles (°): Sb(1)–C(1) 2.200(4), Sb(1)–C(11) 2.223(4), Sb(1)–P(1) 2.531(1), Sb(2)–C(11) 2.221(4), Sb(2)–P(3) 2.516(1), Sb(2)–P(2) 2.529(1), P(1)–C(2) 1.681(4), P(2)–C(2) 1.827(4), P(2)–C(1) 1.874(4), P(3)–C(12) 1.852(4), P(3)–C(1) 1.925(4) P(4)–C(12) 1.689(4), P(4)–C(11) 1.844(4), C(1)–Sb(1)–C(11) 88.7(1), C(1)–Sb(1)–P(1) 91.6(1), C(11)–Sb(1)–P(1) 98.5(1); C(11)–Sb(2)–P(3) 82.6(1), C(11)–Sb(2)–P(2) 96.2(1), P(3)–Sb(2)–P(2) 68.0(4), C(2)–P(1)–Sb(1) 98.8(1), C(2)–P(2)–C(1) 107.6(2), C(2)–P(2)–Sb(2) 104.1(1), C(1)–P(2)–Sb(2) 85.6(1), C(12)–P(3)–C(1) 109.2(2), C(12)–P(3)–Sb(2) 94.7(1), C(1)–P(3)–Sb(2) 84.9(1), P(2)–C(1)–P(3) 95.9(2), P(2)–C(1)–Sb(1) 107.0(2), P(3)–C(1)–Sb(1) 111.8(2), P(1)–C(2)–P(2) 124.9(2), P(4)–C(11)–Sb(2) 107.9(2), P(4)–C(11)–Sb(1) 97.1(2), Sb(2)–C(11)–Sb(1) 109.2(2), P(4)–C(12)–P(3) 121.8(2).

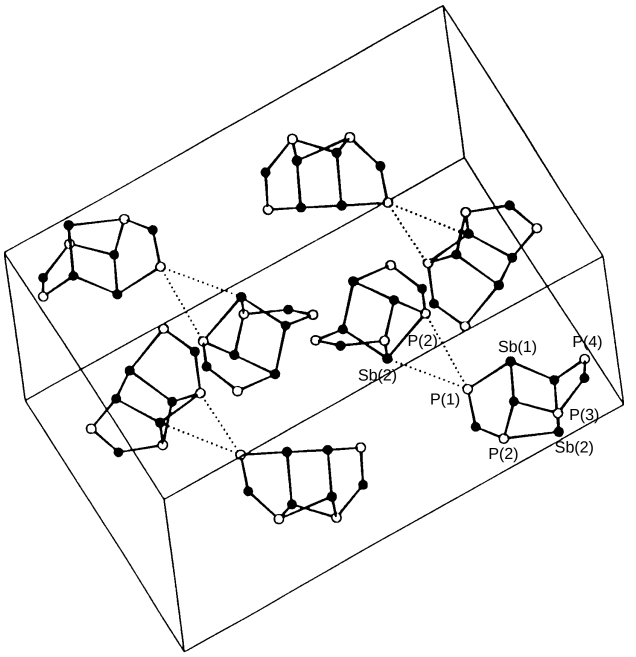


Fig. 2 Unit-cell diagram for $C_4Bu^t{}_4P_4Sb_2$ **6** showing intermolecular interactions. *tert*-Butyl groups omitted for sake of clarity

We have recently discovered that the highly strained cage compound **6** undergoes facile intramolecular rearrangement reactions, either in solution (even at −30 °C) or when treated with transition-metal fragments, *e.g.* $[W(CO)_5]$. The results of these investigations will be presented in a later publication.

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Footnotes

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‡ *Spectroscopic data* for **6**: ^1H NMR (250 MHz, C_6D_6, $SiMe_4$) δ 1.16 (s, 9 H, Bu^t), 1.28 (s, 9 H, Bu^t), 1.48 (s, 9 H, Bu^t), 1.62 (s, 9 H, Bu^t); ^{13}C NMR (100.6 MHz, C_6D_6) δ 30.7 (dd, C*C*H_3, $^3J_{PC}$ 7.5, 7.8 Hz), 31.8 (dd, C*C*H_3, $^3J_{PC}$ 11.4, 10.0 Hz), 32.7 (dd, C*C*H_3, $^3J_{PC}$ 6.0, 9.1 Hz), 36.3 (d, C*C*H_3, $^3J_{PC}$ 10.4 Hz), 38.6 (d, *C*CH_3, $^2J_{PC}$ 16.2 Hz), 42.1 (dd, *C*CH_3, $^2J_{PC}$ 22.0, 21.0 Hz), 46.2 (dd, *C*CH_3, $^2J_{PC}$ 14.9, 12.6 Hz), 47.7 (dd, *C*CH_3, $^2J_{PC}$ 12.1, 14.2 Hz), 79.0 (ddd, PCP, $^1J_{PC}$ 50, 51, $^3J_{PC}$ 8 Hz), 90.5 (d, SbCP, $^1J_{PC}$ 65 Hz), 212.0 (ddd, PCP, $^1J_{PC}$ 77, 74, $^3J_{PC}$ 10.1 Hz), 240.2 (ddd, PCP, $^1J_{PC}$ 89, 87, $^3J_{PC}$ 9.6 Hz); $^{31}P\{^1H\}$ NMR (101.4 MHz, C_6D_6) δ −18.6 (dd, P^2, $^2J_{P2,3}$ 137, $^2J_{P1,2}$ 28 Hz), 32.5 (dd, P^3, $^2J_{P2,3}$ 137, $^2J_{P3,4}$ 31 Hz), 356.5 (d, P^4, $^2J_{P3,4}$ 31 Hz), 363.4 (d, P^1, $^2J_{P1,2}$ 28 Hz); CIMS (70 kV) 645 (MH^+, 8%), 523 (MH^+ − Sb, 10%), 169 (Bu^tCPCBu^{t+}, 15%), 57 (Bu^{t+}, 100%). Suitable analytical data were obtained.

‡ *Crystal data* for **6**: $C_{20}H_{36}P_4Sb_2$, $M = 643.87$, orthorhombic, space group *Pbca*, $a = 12.9730(5)$, $b = 19.0530(7)$, $c = 21.052(2)$ Å, $U = 5203.5(6)$ Å^3, $Z = 8$, $D_c = 1.644$ g cm^{-3}, $F(000) = 2544$, $\mu = 23.26$ cm^{-1}, crystal 0.23 × 0.31 × 0.18 mm, radiation Mo-Kα ($\lambda = 0.71069$ Å), 150(2) K.

All crystallographic measurements were made using a FAST area detector diffractometer. The structure was solved by direct methods and difference synthesis and refined on F^2 by full-matrix least squares using all unique data. All non-hydrogen atoms are anisotropic with H atoms included in calculated positions (riding model). Final wR (on F^2) and R (on F) were 0.0647 and 0.0446 for all data. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/336.

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