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The synthesis and structural characterisation of a diphosphastibolyl potassium complex, $[\{[K(DME)][1,4,2\text{-}P_2SbC_2Bu^t_2]\}_\infty]$, and a novel hetero-cage compound

Cameron Jones *, Ryan C. Thomas

Department of Chemistry, University of Wales, PO Box 912, Park Place, Cardiff, CF10 3TB, UK

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Abstract

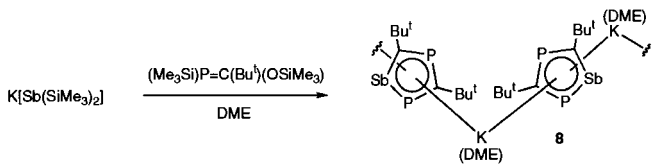
The diphosphastibolyl-potassium complex, $[\{[K(DME)][1,4,2\text{-}P_2SbC_2Bu^t_2]\}_\infty]$, has been prepared from the reaction of $K[Sb(SiMe_3)_2]$ with $(Me_3Si)P{=}C(Bu^t)(OSiMe_3)$. In the solid state it has been shown to exist as an infinite polymer of alternating [K(DME)] and $[\mu\text{-}\eta^5{:}\eta^5\text{-}P_2SbC_2Bu^t_2]$ units. The reaction of two equivalents of this complex with $SiMe_2Cl_2$ has afforded a novel hexahetero-cage compound, $Me_2SiP_4SbC_4Bu^t_4H$, which has been crystallographically characterised.

Keywords: Diphosphastibolyl; Low coordination; Group 15; Cage compound; Heterocycle; Crystal structure

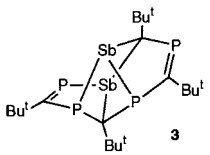
1. Introduction

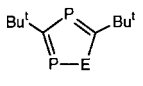
In recent years we have begun to develop the coordination chemistry of the diphosphastibolyl ring anion, $[1,4,2\text{-}P_2SbC_2Bu^t_2]^-$ (**1**). Our interest in this system has largely stemmed from a desire to compare the chemistry of this heterocycle with that of its well established triphospholyl counterpart, $[1,2,4\text{-}P_3C_2Bu^t_2]^-$ (**2**) [1]. We have found that the reactivity of **1** is significantly greater than that of **2**, a fact that could potentially lead to different chemistries for the two anions. Several differences have already been observed in the formation of transition metal complexes of **1**, a field we have explored in some detail [2].

By contrast, the coordination of **1** to main group centres has not been well studied and can be confined to the formation of $[\{Tl(\mu\text{-}\eta^5{:}\eta^5\text{-}P_2SbC_2Bu^t_2)\}_\infty]$ [3] and $[M(C_5Me_5)\eta^5)\text{-}P_2SbC_2Bu^t_2)]$, M = Sn or Pb [4]. Two other surprising results which have been reported in this area are the oxidative coupling of two equivalents of **1** in its reaction with $PbCl_2$ to give the organoantimony cage compound, **3** [5]; and the formation of the chalcogen substituted diphospholes, **4**, by reaction of **1** with $E(S_2CNEt_2)_2$ [6]. We wished to further develop the main group coordination chemistry of **1** by investigating its interaction with alkali metals and tetravalent Group 14 element fragments. The results of these investigations are reported herein.



Scheme 1.





* Corresponding author. Tel.: +44-29-20-874060; fax: +44-29-20-874030.

E-mail address: jonesca6@cardiff.ac.uk (C. Jones).

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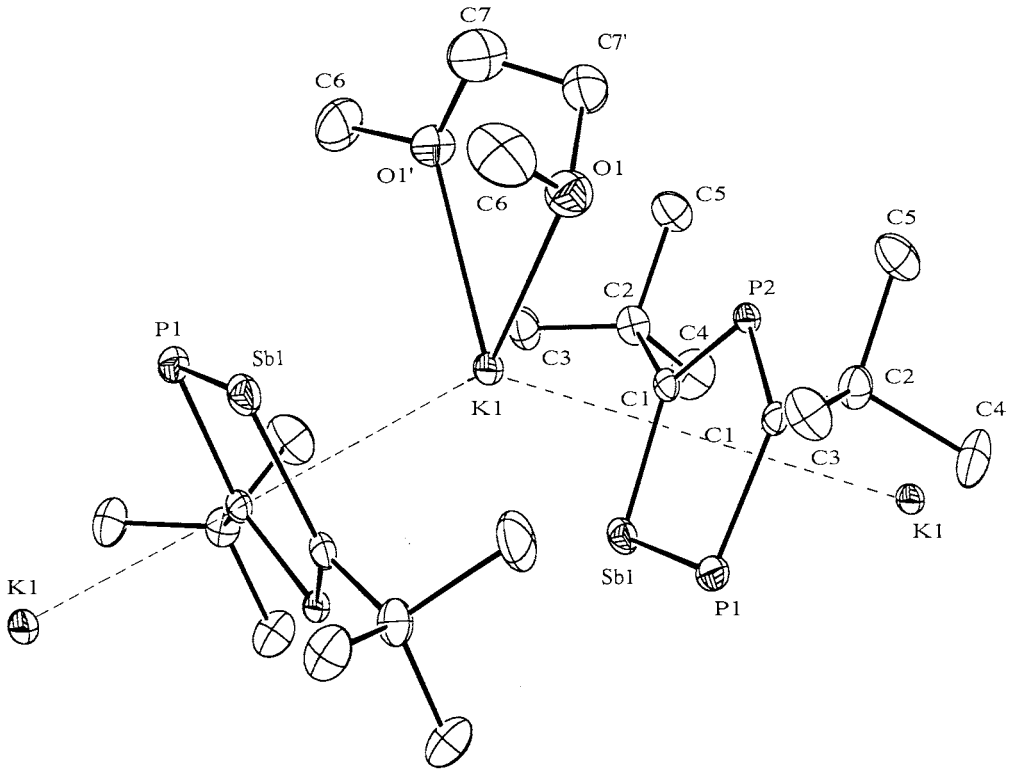


Fig. 1. Molecular structure of **8**.

2. Results and discussion

Although two lithium salts of **1** have been prepared, viz. $[Li(12\text{-crown-4})_2][P_2SbC_2Bu^t_2]$ **5** and $[Li(tmeda)_2][P_2SbC_2Bu^t_2]$ **6** [7], X-ray crystallography has shown the anion in each to have no contact with the cation. By contrast, potassium salts of polyphospholyl anions are known to occur as complexes, e.g. $[\{[K(THF)][1,3\text{-}P_2C_3Bu^t_3]\}_\infty]$ **7** [8], even in the presence of coordinating solvents. We set about to prepare a related potassium complex of **1** by treating $K[Sb(SiMe_3)_2]$, generated in-situ from the reaction of $KOBu^t$ with $Sb(SiMe_3)_3$, with three equivalents of the phosphaalkene, $(Me_3Si)P=C(Bu^t)(OSiMe_3)$, in DME. After 16 h, work-up afforded a low yield (13%) of $[\{[K(DME)][1,4,2\text{-}P_2SbC_2Bu^t_2]\}_\infty]$ **8** (Scheme 1). Following the reaction by ^{31}P-NMR spectroscopy revealed that in the first hour the phosphaalkene was converted to the phosphaalkyne, $P{\equiv}CBu^t$, via. elimination of hexamethyldisiloxane. This process is well documented [1a] as being catalysed by bases which in the present case is $K[Sb(SiMe_3)_2]$. In the following 10 h the generated phosphaalkyne reacted with this base to form **8**. As with the lithium complex, **5**, compound **8** was contaminated with significant amounts (ca. 25%) of the analogous triphospholyl complex, $[\{[K(DME)][1,4,2\text{-}P_3C_2Bu^t_2]\}_\infty]$. Numerous attempts were made to separate the two components by fractional crystallisation but all failed, presumably due to the chemical similarity of the two compounds. In solution, the $^{31}P\{^1H\}$-NMR spectrum of the mixture in DME revealed the characteristic pattern for the triphospholyl anion, $[1,4,2\text{-}P_3C_2Bu^t_2]^-$ [1], and an AX pattern for **8** with two signals at 312 and 281 ppm having a mutual coupling of 55 Hz . These values are very close to those for **6** (309, 288 ppm; $^2J_{PP} = 55$Hz) [7] which suggests that in DME the complex is either largely dissociated or there is a very weak cation–anion interaction.

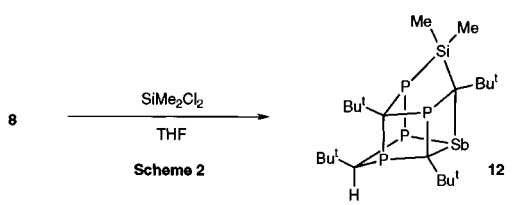
In order to determine the nature of such an interaction in the solid state an X-ray crystal structure analysis on **8** was carried out (Fig. 1, Table 1). It was found that it co-crystallises with its triphospholyl counterpart and as a result the position of each diphosphastibolyl ring anion in the structure was disordered with the triphospholyl anion, $[P_3C_2Bu^t_2]^-$ (ca. 25%). Accordingly, any discussion or inter-ring metrical parameters is meaningless. Despite this positional disorder the X-ray structure determination has revealed the gross molecular framework of the complex. It exists as an infinite polymer consisting of alternating heterocyclic anions and [K(DME)] cations which are approximately η^5-coordinated to adjacent heterocycles in a similar fashion to that seen in the closely related complexes **7** [8] and $[\{Tl(\mu\text{-}\eta^5\text{:}\eta^5\text{-}P_2SbC_2Bu^t_2)\}_\infty]$ [3].

We wished to utilise **8** as a transfer reagent in the formation of tetravalent Group 14 complexes. Our interest in this area has arisen from the recent success that Nixon et al. have had from the reactions of

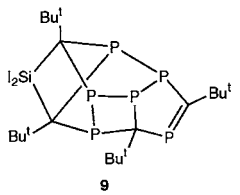
$[K(P_3C_2Bu^t_2)]$ with either SiI_4 or GeI_4 [9]. These afforded the structurally different cage compounds, **9** and **10**, via ring coupling reactions of the presumed intermediates, $[EI_2(\eta^1\text{-}P_3C_2Bu^t_2)]$ E = Si or Ge (**11**). The differences in the chemistries of $[P_2SbC_2Bu^t_2]^-$ and $[P_3C_2Bu^t_2]^-$ are again highlighted by the fact that the reaction of two equivalents of **8** with either SiI_4 or GeI_4 led only to intractable mixtures of many products. As a result the potentially more controllable reaction of **8** with $SiMe_2Cl_2$ was investigated. This led to the formation of the novel hexahetero-cage compound, **12**, in moderate yield (41%) (Scheme 2). Following the reaction by ^{31}P-NMR spectroscopy shed no light on the mechanism of formation of **12** as no intermediates could be observed, even at −40°C. It can, however, be speculated that the mechanism involves the intermediate $[Me_2Si(\eta^1\text{-}P_2SbC_2Bu^t_2)_2]$, c.f. **11**, which undergoes a number of subsequent steps including antimony elimination, cycloaddition reactions and proton abstraction from the solvent, THF. A number of similar proton extractions from solvents have been detailed for complexes containing the triphospholyl anion, **2** [10]. The elimination of antimony in these reactions can be related to the formation of **4** in which antimony is also eliminated from the likely intermediates, $[E(\eta^1\text{-}P_2SbC_2Bu^t_2)_2]$ [6]. The facility of antimony elimination in both reaction types no doubt results from the frailty of the Sb–P multiple bond in **1**. It is noteworthy that the triphospholyl contaminant of **8** appeared to play no part in the formation of **12**.

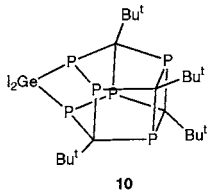
Table 1
Summary of crystallographic data for complexes **8** and **12**

	8	**12**
Formula	$C_{14}H_{28}KO_2P_{2.25}Sb_{0.75}$	$C_{22}H_{43}P_4SbSi$
*M*r	428.46	581.28
Unit cell dimensions		
a (Å)	11.695(2)	13.438(3)
b (Å)	18.016(4)	10.588(2)
c (Å)	9.664(2)	19.038(4)
β (°)	90	94.49(3)
V (Å^3)	2036.2(7)	2692.8(10)
Crystal system	Orthorhombic	Monoclinic
Space group	*Pnma*	$P2_1/c$
λ (Å)	0.71073	0.71073
T (K)	150(2)	150(2)
Z	4	4
Size	0.6 × 0.5 × 0.5	0.2 × 0.2 × 0.2
Color	Yellow	Yellow
μ (cm^{-1})	14.11	13.15
F(000)	876	1200
Reflections collected	3393	5920
R_{int}	0.0315	0.0582
Unique reflections	1902	5437
Parameters varied	144	267
$R[I>2\sigma(I)]$	0.0541	0.0581
R_w (all data)	0.1669	0.1061



Scheme 2.





The $^{31}P\{^1H\}$-NMR spectrum of **12** contains four distinct phosphorus resonances. The highest field signals (δ −55.5 and 10.2 ppm) exhibit a mutual J_{PP} coupling of 256 Hz which is in the expected region for a one bond interaction. These signals have been assigned to P(2) and P(1), respectively (see Fig. 2 for labels). P(3) resonates at 191.3 ppm and displays a $^2J_{P(3)P(1)}$ coupling of 24 Hz. The remaining phosphorus resonance is located at 105.7 ppm and was assigned to P(4). Presumably no two bond couplings between this phosphorus centre and P(2) or P(3) were observed because it forms part of two strained four membered rings and consequently has a high degree of p-character to its bonding with its neighbouring atoms. As expected, the ^{1}H-NMR spectrum for **12** shows four singlets corresponding to the four inequivalent *tert*-butyl groups.

The molecular structure of **12** (Fig. 2, Table 1) is consistent with the solution state NMR data and shows it to be monomeric. All the bond lengths within the cage are normal for single bonded interactions and it is clear that C(6) has been protonated during the reaction. The framework of the cage is similar to that in the previously reported organophosphorus cage, $P_6C_4Bu^t_4H_2$ [11], and appears to be strained. This strain arises from the inclusion of two connecting four membered rings, P(4)C(4)P(3)C(5) and P(4)C(4)Sb(1)C(3), a feature which gives rise to the lack of observable couplings to P(4) (vide supra).

In an attempt to extend this chemistry to the heavier Group 14 elements we have explored the reactions of **8** with $GeMe_2Cl_2$, $SnMe_2Cl_2$ and $SnPh_2Cl_2$. In the first reaction an intractable mixture of many products resulted and in the latter two reactions the known cage compound, **3**, was formed in high yield via oxidative coupling reactions. The work described in this paper has revealed significant differences in the chemistries of the two closely related heterocycles, **1** and **2**. We are currently carrying out studies to elucidate further dif-

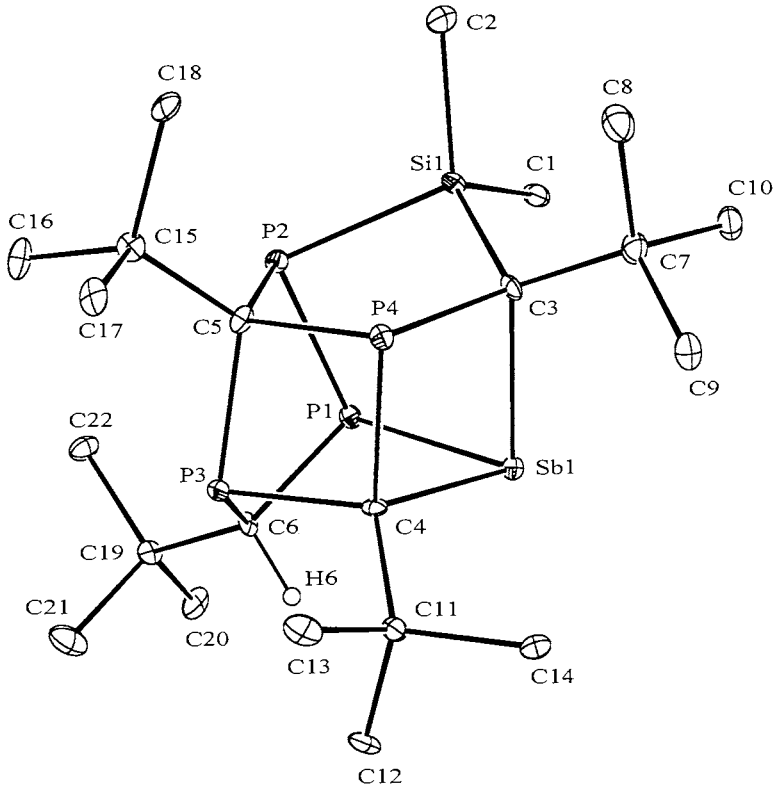


Fig. 2. Molecular structure of **12**. Selected bond lengths (Å) and angles (°): Sb(1)–C(4) 2.223(7), Sb(1)–C(3) 2.236(7), Sb(1)–P(1) 2.5424(19), Sb(1)–P(4) 2.9600(19), P(1)–C(6) 1.870(8), P(1)–P(2) 2.199(3), P(2)–C(5) 1.890(7), P(2)–Si(1) 2.233(3), P(3)–C(4) 1.850(8), P(3)–C(6) 1.877(6), P(3)–C(5) 1.884(7), P(4)–C(3) 1.885(7), P(4)–C(4) 1.896(7), P(4)–C(5) 1.911(7), Si(1)–C(2) 1.861(7), Si(1)–C(1) 1.870(7), Si(1)–C(3) 1.902(8), C(4)–Sb(1)–C(3) 79.2(2), C(4)–Sb(1)–P(1) 89.7(2), C(3)–Sb(1)–P(1) 94.9(2), C(6)–P(1)–P(2) 96.1(2), C(6)–P(1)–Sb(1) 92.5(2), P(2)–P(1)–Sb(1) 99.54(9), C(5)–P(2)–P(1) 99.7(2), C(5)–P(2)–Si(1) 98.3(2), C(4)–P(3)–C(5) 86.1(3), C(4)–P(4)–C(5) 84.1(3), C(2)–Si(1)–C(1) 105.8(4), C(3)–Si(1)–P(2) 99.1(2).

ferences between the two heterocycles, the results of which will form the basis of a future publication.

3. Experimental

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon or dinitrogen. The solvents diethyl ether, hexane, THF and DME were distilled over either potassium or Na/K alloy then freeze/thaw degassed prior to use. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded on either a Bruker AMX360 or Bruker DPX400 spectrometer in C_6D_6 and were referenced to the residual ^{1}H- resonances of the solvent used (^{1}H-NMR) or to external 85% H_3PO_4, 0.0 ppm (^{31}P-NMR). Mass spectra were recorded using a VG Fisons Platform II instrument under APCI conditions. Melting points were determined in sealed glass capillaries under argon, and are uncorrected. Elemental analyses were carried out at the Warwick Analytical Service.

*3.1. [{[K(DME)][1,4,2-$P_2SbC_2Bu^t_2$]}$_\infty$] (**8**)*

To a solution of $Sb(SiMe_3)_3$ (0.9 ml, 2.85 mmol) in DME (20 ml) at −78°C was added KOBu^t (0.34 g, 3 mmol) in DME (20 ml). The solution was warmed to room temperature and stirred for 2 h. The resulting brown solution of $K[Sb(SiMe_3)_2]$ was cooled to −78°C and $(Me_3Si)P=C(Bu^t)(SiMe_3)$ (2.2 ml, 8.6 mmol) added. The resulting solution was warmed to room temperature and stirred overnight before removal of volatiles in vacuo. The oily residue was washed with hexane and extracted with diethyl ether (20 ml). Concentration to ca. 5 ml and storage at −30°C afforded a yellow co-crystallised mixture of **8** and [{[K(DME)][1,2,4-$P_3C_2Bu^t_2$]}$_\infty$] after 7 days. Yield 0.149 g (containing ca. 0.113 g of **8**, 13% yield); M.p. of mixture 112–114°C (dec.); ^{31}P{^{1}H}-NMR (145.78 MHz, DME/C_6D_6) of **8**: δ 312 (d, $^{2}J_{PP}$ 55 Hz, SbPC), 281 (d, $^{2}J_{PP}$ 55 Hz, CPC); ^{1}H- and ^{13}C-NMR spectra could not be confidently assigned due to the nature of the co-crystallised mixture.

3.2. $C_{22}H_{43}P_4SbSi$ (**12**)

A solution of **8** (1.20 g, 2.67 mmol) in THF (15 ml) was added dropwise to a solution of $SiMe_2Cl_2$ (162 μl, 0.17 g, 1.34 mmol) in THF (20 ml) at −78°C. The resulting solution was warmed to room temperature and stirred overnight before volatiles were removed in vacuo. The residue was extracted with hexane (40 ml) and the extract reduced in volume to ca. 5 ml. Cooling to −30°C afforded yellow crystals of **12** (0.32 g, 41%); M.p. 203°C (dec.); ^{1}H-NMR (400 MHz, C_6D_6, 298 K) δ 0.23 (br. s, 6H, $SiMe_2$), 0.45 (s, 1H, CH), 1.02 (s, 9H, Bu^t), 1.27 (s, 9H, Bu^t), 1.31 (s, 9H, Bu^t), 1.39 (s, 9H, Bu^t); ^{31}P{^{1}H}-NMR (145 MHz, C_6D_6, 298 K): δ −55.5 [d, $^1J_{P(1)P(2)}$ 256 Hz, P(2)], 10.2 [dd, $^1J_{P(2)P(1)}$ 256 Hz, $^2J_{P(1)P(3)}$ 24 Hz, P(1)], 105.1 [s, P(4)], 191.3 [d, $^2J_{P(1)P(3)}$ 24 Hz, P(3)]; APCI/MS m/z 582 (M + + H, 100%); Anal. Found: C, 45.32; H, 7.41. Calc. for $C_{22}H_{43}P_4SbSi$: C, 45.46; H, 7.46%.

3.3. Crystallographic studies

All crystallographic measurements were made using an Enraf-Nonius CAD4 diffractometer. The structures of **8** and **12** were solved by direct methods and refined on F^2 by full matrix least squares (SHELX-97) [12] using all unique data. All non-hydrogen atoms are anisotropic with H-atoms included in calculated positions (riding model), except those attached to C(6), C(7) and C(7′) in **8**. Empirical absorption corrections were carried out by the DIFABS method [13]. During the course of the refinement of the structure of **8** it was found that the sites labelled P(1) and Sb(1), which are related by a crystallographic mirror plane, were partially occupied by antimony (37.5%) and phosphorus (62.5%), respectively. The set of atoms O(1) and C(7) (50%) were also found to be disordered with O(1′) and C(7′) (50%). The tertiary butyl methyl carbon atoms C(3), C(4) and C(7) were found to be disordered with C(3′), C(4′) and C(5′) in a 63:37% ratio. These disorders were successfully modelled and the refinement of the structure utilising these partial occupancies was successful.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures of **8** and **12** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 149213 for compound **8** and CCDC no. 149212 for compound **12**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

Acknowledgements

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