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Journal of Organometallic Chemistry 527 (1997) 291–293

Journal of Organometallic Chemistry

Preliminary communication

Synthesis and structural characterisation of the first uncoordinated phosphorus-substituted stibolyl anion

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Received 25 May 1996; revised 19 June 1996

Abstract

The synthesis, crystal and molecular structures of the 2,4-diphosphastibolyl ring anion, $[C_2^tBu_2P_2Sb]^-$, are described.

Keywords: Phosphorus; Antimony; Diphosphastibolyl; Low coordination

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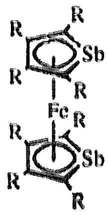
1. Introduction

There is considerable current interest in the chemistry of Group-15-substituted cyclopentadienyl systems [1]. This is typified by the triphospholyl anion, **1**, which has been used in the synthesis of a range of novel organometallic compounds in which the heterocyclic ring displays a variety of coordination modes [2]. The chemistry of the related diphosphaarsolyl anions, **2** and **3**, has recently been initiated but is still in its infancy, presumably because of the low stability of these rings relative to **1** [3]. By extrapolation, it is not surprising that antimony-substituted cyclopentadienyl ring anions are rare and can be confined to a few examples of the general type, $[C_4R_4Sb]^-$, which have mainly found utility in the synthesis of sandwich complexes such as **5** [4]. The remarkable stability of such compounds is believed to result from a high degree of ring aromaticity. These results have encouraged us to extend this work to an examination of phosphorus-substituted stibolyl anions which were unknown prior to this study. Herein we report the synthesis and characterisation of the first 2,4-diphosphastibolyl ring anion, $[C_2^tBu_2P_2Sb]^-$ **4**, the X-ray crystal structure of which represents the first of any uncoordinated stibolyl anion. It should be noted that in a concurrent publication we have reported the use of **4** in the formation of the sandwich complexes $[Ru(\eta^5\text{-}C_5R_5)(\eta^5\text{-}C_2^tBu_2P_2Sb)]$, R = H, Me [5].

E = P E' = P **1**
E = As E' = P **2**
E = P E' = As **3**
E = Sb E' = P **4**



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2. Results and discussion

Treatment of a DME solution of $Li[Sb(SiMe_3)_2]$ with either the phosphaalkyne, $P\equiv C^tBu$, or the phosphaalkene, $(Me_3Si)P{=}C(^tBu)(OSiMe_3)$, followed by treatment with either TMEDA or 12-crown-4 yields a mustard-coloured powder which was shown by $^{31}P\{^1H\}$ NMR spectroscopy to contain two components (Scheme 1). The major component in both reactions (ca. 75% by NMR) displays an AX pattern (δ 277.9, 308.5 ppm) with a characteristic $^2J_{P(A)P(X)}$ coupling (55 Hz) and was assigned to **4**. The low field signal in this pattern was significantly broadened, which strongly suggests it originates from the ring phosphorus adjacent to the quadrupolar antimony centre. The minor component (ca. 25%) exhibited the pattern characteristic of the known

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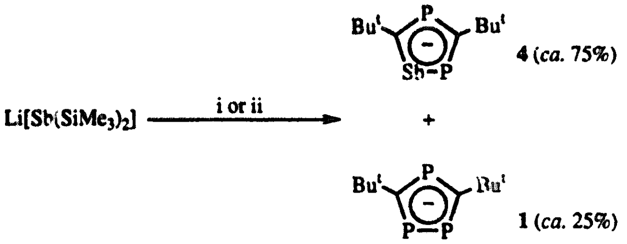
PII S0022-328X(96)06598-9



Scheme 1. Reagents and conditions: (i) P ≡ C^{t}Bu, DME, 25°C, 72 h; (ii) $(Me_3Si)P=C^tBu(OSiMe_3)$, DME, 25°C, 72 h.

triphospholyl anion **1**. A similar co-formation of **1** has previously been seen in the preparation of the related heterocycles **2** and **3** [3]. It is noteworthy that when the present reaction was carried out with $(Me_3Si)P=C^tBu(OSiMe_3)$, NMR monitoring revealed that the phosphaalkene was totally converted to the phosphaalkyne, $P\equiv C^tBu$, in the first hour, presumably via a base-catalysed (i.e. $Li[Sb(SiMe_3)_2]$) elimination of hexamethyldisiloxane. The generated phosphaalkyne then reacted with $Li[Sb(SiMe_3)_2]$ over the ensuing 3 days to form **4**. Interestingly, the preparation of the analogous diphosphaarsolyl anions, **2** and **3**, could only be carried out by the treatment of $Li[As(SiMe_3)_2]$ with $P\equiv C^tBu$ and not $(Me_3Si)P=C^tBu(OSiMe_3)$.

Another feature of the synthesis of $[C_2^tBu_2P_2Sb]^-$ is that it is regioselective, yielding only the 2,4-isomer, **4**. This is in contrast to the analogous preparation of $[C_2^tBu_2P_2As]^-$ which yields an approximately equimolar mixture of the 2,4- and 3,4-isomers, **2** and **3** respectively [3]. One cannot be sure why this is so, but perhaps it indicates that P=Sb multiple bonding may be preferred over purely C=Sb multiple bonding.

The structure of [**4**][Li(12-crown-4)$_2$] was confirmed by a single crystal X-ray diffraction study (see Section 3.1) (Fig. 1). Although the compound crystallises with two independent molecules in the asymmetric unit there are no significant geometric differences between them.

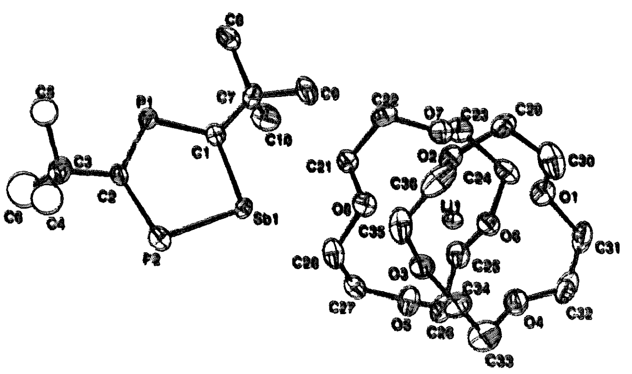


Fig. 1. Structure of one molecule in the asymmetric unit of [**4**][Li(12-crown-4)$_2$]. Selected bond lengths (Å) and angles (deg): Sb(1)–P(2) 2.346(2), Sb(1)–C(1) 2.039(11), P(1)–C(1) 1.722(10), P(1)–C(2) 1.782(11), P(2)–C(2) 1.885(11), C(1)–Sb(1)–P(2) 94.6(3), C(2)–P(2)–Sb(1) 98.2(3), C(1)–P(1)–C(2) 105.2(5), P(1)–C(1)–Sb(1) 120.0(6), P(1)–C(2)–P(2) 121.8(5).

During the course of refinement it was found that [**4**][Li(12-crown-4)$_2$] (78%) co-crystallises with [**1**][Li(12-crown-4)$_2$] (22%), which is consistent with the NMR of the reaction mixture (vide supra). In addition, there is considerable site disorder between the antimony centres and the phosphorus centres in the 2-positions of both rings in the asymmetric unit. Consequently, it is not valid to comment on the bond lengths and angles within either ring, though it is clear that they are essentially planar. The geometry of the [Li(12-crown-4)$_2$] cations is very similar to that seen in related compounds, e.g. $[SbPh_2]$[Li(12-crown-4)$_2$] [6].

We are currently exploring the use of **4** as a ligand in the synthesis of a range of sandwich and half-sandwich organometallic complexes, the results of which will be reported in forthcoming publications.

3. Experimental details

[**4**][Li(TMEDA)$_2$]: In a typical experiment $(Me_3Si)P=C(^tBu)(OSiMe_3)$ (6.2 g, 23.7 mmol) was added over 10 min to a solution of $Li[Sb(SiMe_3)_2]$ (1.58 g, 5.75 mmol) in DME 30 ml at −40°C. The solution was warmed to room temperature and stirred for 3 days in the absence of light. Removal of volatiles in vacuo afforded a brown oil which was washed with hexane (3 × 50 ml). The resulting oily solid was treated with TMEDA (10 ml), volatiles removed in vacuo, and the residue washed with hexane (3 × 50 ml) to afford a mixture of [**4**][Li(TMEDA)$_2$] and [**1**][Li(TMEDA)$_2$] as a mustard-coloured powder. Yield 2.02 g, m.p. 95–105°C (dec.). Using $P\equiv C^tBu$ in place of $(Me_3Si)P=C(^tBu)(OSiMe_3)$, or 12-crown-4 in place of TMEDA did not significantly affect the yield.

3.1. Crystal data for [4][Li(12-crown-4)$_2$]

$C_{52}H_{100}Li_2O_{16}P_{4.45}Sb_{1.55}$ $M = 1321.73$ triclinic, space group $P\bar{1}$, $a = 13.440(2)$ $b = 17.2212(13)$, $c = 17.4648(9)$ Å, $\alpha = 116.98(4)$, $\beta = 99.19(2)$, $\gamma = 106.974(11)°$, $V = 3236.6(5)$ Å^3, $Z = 4$, $D_c = 1.356$ g cm^{-3}, $F(000) = 1384$, $\mu = 8.20$ cm^{-1}, crystal 0.18 × 0.22 × 0.20 mm^3, radiation Mo Kα ($\lambda = 0.71069$ Å), 150(2) K.

All crystallographic measurements were made using a FAST area detector diffractometer following previously described procedures [7]. The structure was solved by direct methods (SHELXS86) [8] and difference synthesis and refined on F^2 by full matrix least squares (SHELX93) [9] using all unique data. All non-hydrogen atoms are anisotropic except C(4)–C(6) and C(18)–C(20), which were refined isotropically with all H-atoms included in calculated positions (riding model). Final R (on F^2) and wR (on F) were 0.0714 and 0.1773 for $I > 2\sigma(I)$. Full details of data collection, structure refinement, atomic coordinates, thermal parameters and bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

Acknowledgements

We thank the University of Wales (Studentship for MDF).

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