The first diphosphastibolyl complexes: synthesis and characterisation of [Ru(η5-C5R5)(η5-C2But2P2Sb)]; R = H or Me

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Treatment of the novel ring anion [C2But2P2Sb]− 4 with [Ru(η5-C5R5)(MeCN)3]PF6, (R = H, Me), affords the compounds [Ru(η5-C5R5)(η5-C2But2P2Sb)] (R = H 6, Me 7), which represent the first examples of complexes derived from a diphosphastibolyl ring; the X-ray crystal structure of 7 is described.

The chemistry of phosphorus-substituted cyclopentadienyl ring systems, $C_nR_nP_{5-n}$ (n = 0–4), is a rapidly expanding area[1] perhaps best exemplified by the triphospholyl anion, 1, the organometallic chemistry of which has been extensively investigated.[2] Recently, this field has been extended to the less stable 2,4- and 3,4-diphosphaarsolyl ring anions, 2 and 3,[3] which are obtained as a mixture from the reaction of [Li{As(SiMe3)2}(dme)] with 2 equiv. of the phosphaalkyne, P≡CBut. Not surprisingly, the analogous phosphorus-substituted stibolyl ring systems have remained elusive prior to this work, presumably due to the instability inherent in low-coordination antimony compounds. Indeed, compounds containing a two-coordinate antimony centre can be confined to a handful of examples, most of which have arisen from the pioneering work of Ashe who has explored the chemistry of complex types such as 5, derived from stibolyl anions [C4R4Sb]−.[4] Such complexes are thought to be stabilised by considerable aromaticity within the stibolyl ring.

E = P   E′ = P   1
E = As E′ = P   2
E = P   E′ = As 3
E = Sb E′ = P   4

5
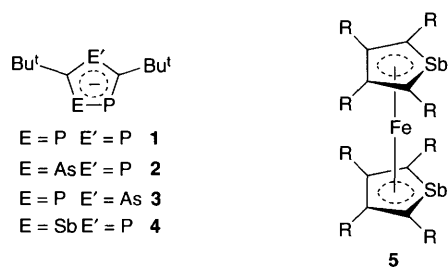
These results prompted us to initiate the chemistry of phosphorus-substituted stibolyl ring anions which we have achieved with the high yielding, regioselective synthesis of the 2,4-diphosphastibolyl anion, 4, via the treatment of [Li{Sb-(SiMe3)2}(dme)] with either P≡CBut or the phosphaalkene, (Me3Si)P=CBut(OSiMe3).[5] Herein we report (i) the synthesis of the first complexes derived from a phosphorus-substituted stibolyl ring and (ii) the first structural characterisation of a phosphorus-substituted stibolyl ring.

Treatment of 4[Li(tmeda)2] with [Ru(η5-C5R5)(MeCN)3]PF6 (R = H, Me), led to the air- and moisture-stable, orange–red sandwich complexes, 6 and 7 respectively (Scheme 1). Both complexes could be partially purified by recrystallisation from hexane or sublimation (185 °C, 0.1 mmHg, 6; 175 °C, 0.1 mmHg, 7) but could not be obtained in a totally pure state due to contamination with small amounts (ca. 10%) of the known complexes [Ru(η5-C5R5)(η5-C2But2P3)], R = H, 8[6] (in 6) or Me, 9[6] (in 7). This contamination arises from the triphospholyl anion, 1, which is an unavoidable by-product in the synthesis of

4. The approximate yields of 6 (38%) and 7 (37%) were determined by integration of the 1H NMR spectra of the mixtures (6 and 8) and (7 and 9). The remarkable thermal stability of 6 and 7, which decompose only at temperatures >220 °C, is presumably due to a high degree of aromaticity within 4 as has been suggested for the related stibolyl rings in 5 (vide supra).[4]

The spectroscopic data† for 6 and 7 are similar and support the proposed structures. Their 31P{1H} NMR spectra display AX patterns with characteristic $^2J_{PAPX}$ couplings. The broadness of the low-field signals suggests that these originate from the ring phosphorus atoms adjacent to the quadrupolar antimony centres. Both the 1H and 13C NMR spectra of 6 and 7 are as expected and highlight inequivalent tertiary butyl groups. The mass spectra of both compounds exhibit molecular-ion peaks with the correct isotopic distributions, and similar fragmentation patterns to those for the related compounds, 8 and 9.

The molecular structure‡ of 7 is depicted in Fig. 1. During the course of refinement it was found that the site labelled Sb is partially occupied (10%) by phosphorus while the sites P(1) and P(2) have a 100% phosphorus occupancy. This observation is consistent with the solution NMR data and confirms that 9 (10%) cocrystallises with 7 (90%). Therefore, Fig. 1 also represents the first structural characterisation of 9. Because of the site disorder at Sb it is not valid to comment on the bond lengths and angles within the diphosphastibolyl ring. However, from the structure it is clear that both rings are planar, η5-ligated to the ruthenium centre and almost parallel (dihedral angle 2°). Interestingly, the distance from the ruthenium atom to the C2But2P2Sb ring centroid [1.786(3) Å] is considerably less than to the C5Me5 ring centroid [1.847(4) Å], the centroid–Ru–centroid angle being close to linear at 177°. It is noteworthy that the structural characterisation of 7 is the first of any complex containing a delocalised double bond between phosphorus and antimony centres.

Another interesting feature of the structure became evident from an examination of the unit cell (Fig. 2) which shows a close contact [3.467(3) Å] between a pair of centrosymmetrically related P(2) atoms. This is significantly less than the sum of the van der Waals radii for two phosphorus centres (3.80 Å) and generates a pseudo-dimeric structure binding both enantiomers

4 ——i——>

6 R = H
7 R = Me
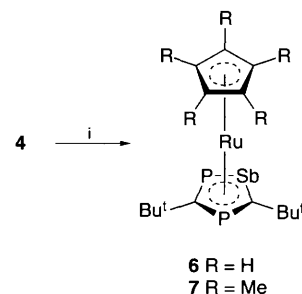
Scheme 1 Reagents and conditions: i, [Ru(η5-C5R5)(MeCN)3][PF6] (R = H, Me), dme, 24 h, 25 °C

of **7**. To the best of our knowledge such intermolecular contacts have not previously been observed in any sandwich complexes derived from the ring anions **1–3**. However, they can be compared to the very weak intermolecular P···P interactions previously observed in diphosphanes, R_2PPR_2,[7] which themselves are analogous to the much stronger inter- and intramolecular Sb···Sb contacts in distibanes, R_2SbSbR_2,[7] and some stibolyl complexes, **5**,[4] respectively.
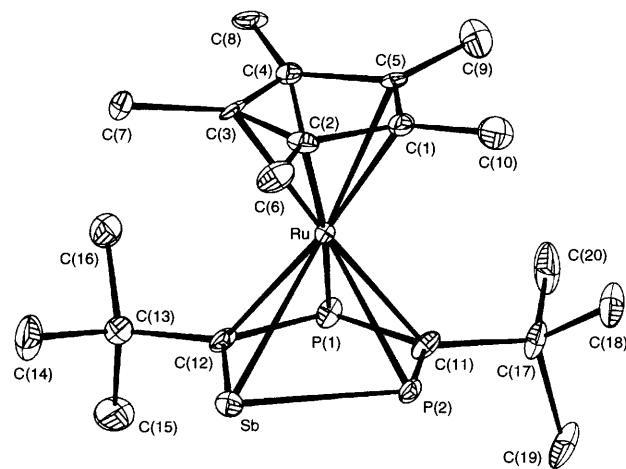

Fig. 1 Molecular structure of **7**. Selected bond lengths (Å) and angles (°): Sb–C(12) 2.102(9), Sb–P(2) 2.426(2), P(1)–C(12) 1.751(9), P(1)–C(11) 1.757(9), P(2)–C(11) 1.793(9), Ru–Sb 2.7128(10), Ru–P(1) 2.419(2), Ru–P(2) 2.472(2), Ru–C(11) 2.273(8), Ru–C(12) 2.310(8); C(12)–Sb–P(2) 88.5(2), C(12)–P(1)–C(11) 101.4(4), C(11)–P(2)–Sb 100.2(3), P(1)–C(11)–P(2) 126.0(5), P(1)–C(12)–Sb 123.5(4).
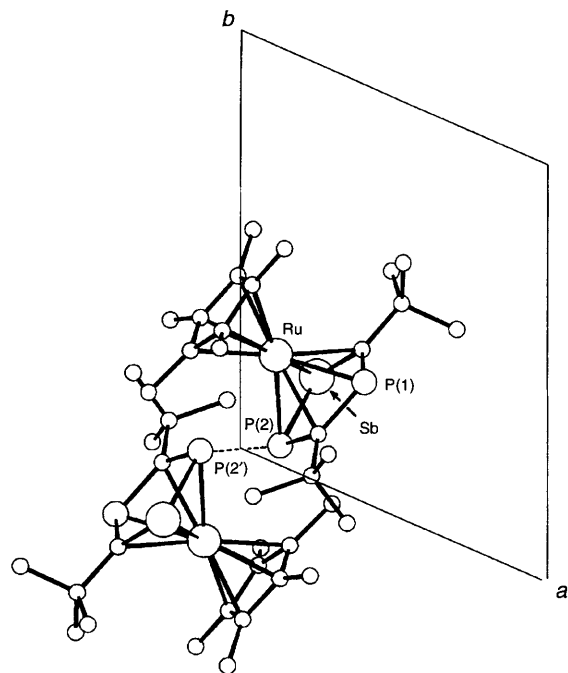

Fig. 2 Unit-cell diagram of **7** showing intermolecular interaction

We have recently extended this work to a study of the tetraphospha-distiba-ferrocene and -ruthenocene complexes, $[M(\eta^5\text{-}C_2Bu^t_2P_2Sb)_2]$ (M = Fe, Ru), the results of which will be presented in a later publication.

Footnotes

† *Spectroscopic data*: **6**: ^{1}H NMR (250 MHz, C_6D_6, SiMe$_4$) δ 1.24 (s, 9 H, Bu^t), 1.44 (s, 9 H, Bu^t), 4.65 (s, 5 H, C_5H_5); ^{13}C NMR (100.6 MHz, C_6D_6) δ 36.6 [d of d, C(CH$_3$)$_3$, $^3J_{PC}$ 10.5, 10.5 Hz], 38.6 [d, C(CH$_3$)$_3$, $^3J_{PC}$ 10.6 Hz], 40.2 [d of d, C(CH$_3$)$_3$, $^2J_{PC}$ 19.4, 15.4 Hz], 40.9 [d, C(CH$_3$)$_3$, $^2J_{PC}$ 16.9 Hz], 76.6 (s, C_5H_5), 140.7 (d of d, PCP, $^1J_{PC}$ 86.2, 110.7 Hz), 149.6 (d, SbCP, $^1J_{PC}$ 84.3 Hz); ^{31}P{^{1}H} NMR (101.4 MHz, C_6D_6) δ 27.8 (d, CPC, $^2J_{PP}$ 35.6 Hz), 64.7 (d, SbPC); EIMS (70 kV) m/z 488 (M$^+$, 10%) 350 [M$^+$ − (CBu^t)$_2$, 48%], 57 (Bu^{t+}, 100%). **7**: ^{1}H NMR (250 MHz, C_6D_6, SiMe$_4$) δ 1.45 (s, 9 H, Bu^t), 1.60 (s, 9 H, Bu^t), 1.83 (s, 15 H, C_5Me_5); ^{13}C NMR (100.6 MHz, C_6D_6) δ 13.9 [s, C_5Me_5], 36.8 [d of d, C(CH$_3$)$_3$, $^3J_{PC}$ 10.7, 10.7 Hz], 38.6 [d, C(CH$_3$)$_3$, $^3J_{PC}$ 10.8 Hz], 41.2 [d of d, C(CH$_3$)$_3$, $^2J_{PC}$ 19.1, 15.7 Hz], 41.9 [d, C(CH$_3$)$_3$, $^2J_{PC}$ 17.7 Hz], 93.1 (s, C_5Me_5), 142.1 (d of d, PCP, $^1J_{PC}$ 83.5, 108.2 Hz), 152.9 (d, SbCP, $^1J_{PC}$ 82.3 Hz); ^{31}P{^{1}H} NMR (101.4 MHz, C_6D_6) δ 30.1 (d, CPC, $^2J_{PP}$ 41.4 Hz), 80.0 (d, SbPC); EIMS (70 kV) m/z 558 (M$^+$, 10%), 420 [M$^+$ − (CBu^t)$_2$, 12%], 57 (Bu^{t+}, 100%).

‡*Crystal data for* **7**: $C_{20}H_{33}P_{2.10}RuSb_{0.9}$, M = 549.15, triclinic, space group $P\bar{1}$, a = 8.7410(9) b = 10.535(2), c = 13.880(3) Å, α = 96.590(13), β = 106.970(10), γ = 110.230(11)°, U = 1113.5(3) Å^3, Z = 2, D_c = 1.638 g cm^{-3}, $F(000)$ = 549, μ = 19.24 cm^{-1}, crystal 0.24 × 0.22 × 0.18 mm, radiation Mo-Kα (λ = 0.710 69 Å), 150(2) K.

All crystallographic measurements were made using a FAST area detector diffractometer following previously described procedures.[8] The structure was solved by direct methods (SHELXS86)[9] and difference synthesis and refined on F^2 by full-matrix least squares (SHELX93)[10] using all unique data. All non-hydrogen atoms are anisotropic with H atoms included in calculated positions (riding model). Final R (on F) and wR (on F^2) were 0.0659 and 0.1510 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 182/126.

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