

Carbon–antimony bond fission in reactions of triphenylantimony with palladium(II): crystal structures of *trans*-chloro(phenyl) bis(triphenylantimony) palladium(II) and *trans*-bromo(phenyl) bis(triphenylantimony) palladium(II)

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Abstract

Triphenylantimony reacts with $[\text{PdX}_2\text{cod}]$ ($\text{X} = \text{Cl}$ or Br ; $\text{cod} = \text{cyclo-octa-1,5-diene}$) in refluxing dichloromethane to give the palladium phenyl complexes *trans*- $[\text{PdXPh}(\text{SbPh}_3)_2]$. Treatment of palladium(II) chloride with triphenylantimony in refluxing acetone–diethyl ether solution also gives *trans*- $[\text{PdClPh}(\text{SbPh}_3)_2]$, but reaction of palladium(II) bromide with triphenylantimony affords *cis*- $[\text{PdBr}_2(\text{SbPh}_3)_2]$. A small amount of *trans*- $[\text{PdClPh}(\text{SbPh}_3)_2]$ is present in samples of *cis*- $[\text{PdCl}_2(\text{SbPh}_3)_2]$ prepared from the reaction of Na_2PdCl_4 with triphenylantimony in aqueous acetone–diethyl ether. The single crystal X-ray structures of *trans*- $[\text{PdXPh}(\text{SbPh}_3)_2]$ ($\text{X} = \text{Cl}$ or Br) are described.

Keywords: Palladium(II); Crystal structures; Triphenylantimony; Tetrahydrofuran (THF)

1. Introduction

Reaction of triphenylantimony with palladium(II) acetate in tetrahydrofuran at 47°C has been shown to result in antimony–phenyl bond cleavage to give the palladium(II)–phenyl complex $[\text{Pd}_3\text{Ph}_2(\text{OAc})_4(\text{SbPh}_3)_2]$ [1]. Treatment of triphenylantimony with palladium(II) chloride at temperatures above 100°C has also been shown to afford benzene, biphenyl and chlorobenzene [2], and under pressures of carbon dioxide or a mixture of carbon monoxide and nitrogen monoxide the palladium(II) catalysed antimony–phenyl bond cleavage of triphenylantimony has been shown to afford benzoic acid [3]. The reaction of triphenylantimony with hydrated rhodium(III) chloride in refluxing ethanol is known to afford the rhodium–phenyl complex $[\text{RhPhCl}_2(\text{SbPh}_3)_3]$ along with *mer*- $[\text{RhCl}_3(\text{SbPh}_3)_3]$ [4]. Herein we report that treatment of some palladium(II) halide complexes with triphenylantimony under mild conditions also results in antimony–carbon

bond cleavage. Organo–metal bond cleavage in SbR_3 compounds has also been shown to occur in reactions with electrophiles, e.g. halogens, HgCl_2 , MCl_3 ($\text{M} = \text{As}$, Sb , Bi), free radicals, and alkali metals [5,6]. Antimony–carbon bond cleavage has also been observed in reactions of the halides Ph_3SbX_2 [7].

2. Results and discussion

During an investigation of the reaction of palladium(II) complexes with triphenylantimony, we observed that treatment of $[\text{PdCl}_2\text{cod}]$ ($\text{cod} = \text{cyclo-octa-1,5-diene}$) with triphenylantimony in refluxing dichloromethane afforded a bright yellow complex, *trans*- $[\text{PdClPh}(\text{SbPh}_3)_2]$ (**1**), characterised on the basis of microanalysis, IR and ^1H NMR spectroscopic data together with a single crystal X-ray determination as the phenyl palladium complex. Similarly, reaction of triphenylantimony with $[\text{PdBr}_2\text{cod}]$ afforded the corresponding bromo complex *trans*- $[\text{PdBrPh}(\text{SbPh}_3)_2]$ (**2**).

The molecular structure of complex **1** is shown in Fig. 1, which also gives the crystallographic numbering

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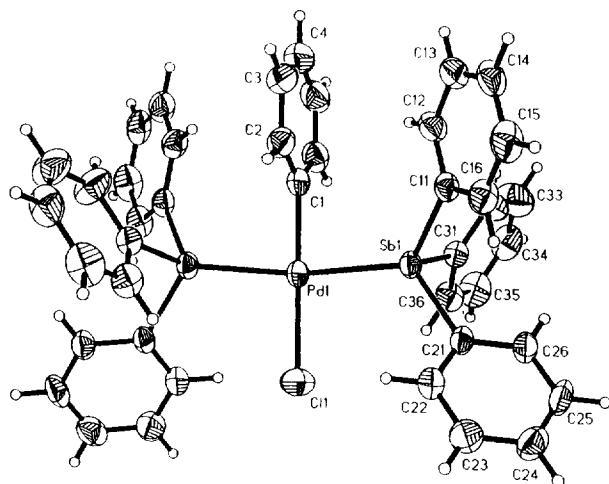


Fig. 1. Molecular structure of **1** showing the atom numbering scheme. Displacement parameters are shown at the 30% level.

scheme. Selected bond distances and angles are given in Table 1. The geometry at the palladium in **1** is square-planar with *trans* antimony donors and phenyl *trans* to chlorine, and there is a crystallographic two-fold axis through Pd(1), Cl(1), C(1), C(4). The Pd–Sb distance (2.557(5) Å) is similar to those in the palladium(II) triphenylantimony complexes *trans*-[PdI₂(SbPh₃)₂] [8] (2.578(1) Å), [Pd₂(OAc)₄(SbPh₃)₂] [1] (2.508(4) Å), [Pd₃Ph₂(OAc)₄(SbPh₃)₂] [1] (2.473(4) Å). The Pd–C(1) distance (2.016(7) Å) is also similar to that found in the related complex *trans*-[PdClPh(PCy₃)₂] (**3**) [9] (2.004(6) Å), but the Pd–Cl distance in **1** (2.373(2) Å) is shorter than that found in the complex **3** (2.403(1) Å).

Complex **2** is isostructural with complex **1**, with a Pd–Sb distance of 2.5421(5) Å. The Pd–Br distance of 2.491(2) Å is similar to that in the complex *trans*-[PdBr(1,3-C₆H₂F₂CH=NC₆H₅)(PPh₃)₂] (**4**) (2.486(1) Å) [10]. The Pd–Cl and Pd–Br distances in **1** and **2** are both longer than those found in the ions [PdCl₄]²⁻ [11] (2.318 Å) and [PdBr₄]²⁻ [12] (2.444(3) Å) respectively, consistent with the *trans* influence of a phenyl group.

The reaction of triphenylantimony with [PdX₂cod]

provides a convenient synthesis of the phenyl complexes *trans*-[PdXPh(SbPh₃)₂], (X = Cl or Br). Interestingly, we also find that the literature synthesis [13] of *cis*-[PdCl₂(SbPh₃)₂], which involves the reaction of triphenylantimony with Na₂PdCl₄ in aqueous acetone–diethyl ether, afforded samples of *cis*-[PdCl₂(SbPh₃)₂] which contained the phenyl complex **1**. Thus, the ¹H NMR spectrum of the complex contained a two-proton and three-proton multiplet at 7.11 and 6.66 ppm, which can be assigned to aromatic protons of the phenyl on palladium. The aromatic protons of the SbPh₃ ligands appeared in the range 7.5 to 7.2 ppm. Integration of these signals indicated that a sample of *cis*-[PdCl₂(SbPh₃)₂], prepared from a 2:1 molar ratio of SbPh₃ and Na₂PdCl₄ in aqueous acetone–diethyl ether at room temperature, contained about 8% complex **1**, which is increased to about 23% in refluxing aqueous acetone–diethyl ether. Using 3 mol triphenylantimony at room temperature the sample of *cis*-[PdCl₂(SbPh₃)₂] contained about 40% **1**. Interestingly, treatment of PdBr₂ with triphenylantimony in aqueous acetone–diethyl ether at room temperature afforded only *cis*-[PdBr₂(SbPh₃)₂] (**5**).

Recent studies have shown that photolysis of [PdCl₂(Ph₂SbCH₂SbPh₂)₂] generates the dimeric phenyl complex [Pd₂(μ-Ph₂SbCH₂SbPh₂)₂Ph₂Cl₂] [14]. However, we find that the reaction of triphenylantimony with [PdX₂cod] is not light-sensitive. [PdXPh(SbPh₃)₂] appears stable in light.

3. Experimental

All reactions were performed under a dry, oxygen-free, nitrogen atmosphere, using solvents which were dried and distilled under nitrogen just prior to use. Microanalyses were carried out by Butterworth Laboratories Ltd., Teddington, Middlessex. Melting points were measured on a Reichert hot stage apparatus and are uncorrected. The FAB mass spectra of the solid complexes were obtained on a Kratos Concept double

Table 1

Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses for **1** and **2**

1		2	
Sb(1)–Pd(1)	2.5568(5)	Sb(1)–Pd(1)	2.5421(5)
Pd(1)–C(1)	2.016(7)	Pd(1)–C(1)	2.03(2)
Pd(1)–Cl(1)	2.373(2)	Pd(1)–Br(1)	2.491(2)
Sb(1)–C(31)	2.131(6)	Sb(1)–C(31)	2.139(7)
Sb(1)–C(21)	2.122(4)	Sb(1)–C(21)	2.124(9)
Sb(1)–C(11)	2.130(5)	Sb(1)–C(11)	2.135(9)
C(1)–Pd–Cl(1)	180.0	C(1)–Pd–Br(1)	180.0
Sb(1)–Pd–Sb(1) #1	171.36(2)	Sb(1)–Pd–Sb(1) #1	170.38(5)
C(1)–Pd–Sb(1)	85.68(1)	C(1)–Pd–Sb(1)	85.19(2)
Cl(1)–Pd–Sb(1)	94.32(1)	Br(1)–Pd–Sb(1)	94.81(2)

#1 symmetry operation 1 – x, y, 0.5 – z.

focusing sector mass spectrometer. The ^1H NMR spectra were recorded at room temperature in $[\text{}^2\text{H}_1]\text{chloroform}$ on a Bruker ARX 250 spectrometer operating at 250.13 MHz with SiMe_4 (0.0 ppm) as internal reference. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at room temperature in $[\text{}^2\text{H}_1]\text{chloroform}$ on a Bruker ARX 250 spectrometer operating at 62.9 MHz in CDCl_3 . The quoted IR spectra were recorded on a Perkin–Elmer 580B spectrophotometer in Nujol mulls between polythene plates in the range 600–200 cm^{-1} .

The compounds $[\text{PdCl}_2\text{cod}]$ [15], $[\text{PdBr}_2\text{cod}]$ [15], and *cis*- $[\text{PdCl}_2(\text{SbPh}_3)_2]$ [13] were prepared as described in the literature. Triphenylantimony was purchased from Aldrich.

3.1. Reaction of triphenylantimony with $[\text{PdCl}_2(\text{cod})]$

Triphenylantimony (0.3 g, 0.85 mmol) in dichloromethane (2 cm^3) was added to a solution of $[\text{PdCl}_2\text{cod}]$ (0.1 g, 0.35 mmol) in dichloromethane (8 cm^3) and the solution was refluxed for 4 h. The solution was cooled to room temperature and diethyl ether (10 cm^3) was added; after several days fine bright yellow crystals of **1** were deposited. The filtered product was washed with diethyl ether and dried in vacuo. Yield 0.110 g (35% based on Pd). Anal. Found: C, 54.1; H, 3.7; Cl, 3.8. $\text{C}_{42}\text{H}_{35}\text{ClPdSb}_2$ Calc.: C, 54.5; H, 3.8; Cl, 3.8%. M.p. 165–170 °C (decomp.). IR: $\nu(\text{Pd–Cl})$ 270 cm^{-1} . Mass spectrum: $[\text{M} - \text{Cl}]^+$ at m/z 889. ^1H NMR: $\delta(\text{ppm})$ 7.41–7.24 (30H, m, Ph–Sb), 6.96 (2H, m, Ph–Pd), 6.58 (3H, m, Ph–Pd). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta(\text{ppm})$ 139.6, 136.3, 131.9, 131.2, 129.7, 128.9, 128.3, 123.

3.2. Reaction of triphenylantimony with $[\text{PdCl}_2]$

A solution of triphenylantimony (1.5 g, 4.3 mmol) in diethyl ether (5 cm^3) was added to a suspension of PdCl_2 (0.3 g, 1.7 mmol) in acetone (25 cm^3) and stirred for 1 h. The pale yellow solid was filtered off, washed with diethyl ether and dried in vacuo. Recrystallisation from dichloromethane–diethyl ether gave fine bright yellow crystals of **1**. Yield 0.980 g (63% based on Pd). Anal. Found: C, 54.5; H, 3.7; Cl, 3.8. $\text{C}_{42}\text{H}_{35}\text{ClPdSb}_2$ Calc.: C, 54.5; H, 3.8; Cl, 3.8%. M.p. 165–170 °C (decomp.). IR: $\nu(\text{Pd–Cl})$ 270 cm^{-1} . Mass spectrum: $[\text{M} - \text{Cl}]^+$ at m/z 889. ^1H NMR: $\delta(\text{ppm})$ 7.41–7.27 (30H, m, Ph–Sb), 6.96 (2H, m, Ph–Pd), 6.58 (3H, m, Ph–Pd). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta(\text{ppm})$ 139.6, 136.3, 131.9, 131.2, 129.8, 128.9, 128.3, 123.

3.3. Reaction of triphenylantimony with $[\text{PdBr}_2(\text{cod})]$

Triphenylantimony (0.2 g, 0.56 mmol) and $[\text{PdBr}_2\text{cod}]$ (0.05 g, 0.13 mmol) similarly gave compound **2** (yield 0.092 g, 71%). Anal. Found: C, 51.9; H, 3.6; Br, 7.9.

$\text{C}_{42}\text{H}_{35}\text{BrPdSb}_2$ Calc.: C, 52.0; H, 3.6; Br, 8.3%. M.p. 198–200 °C (decomp.). $[\text{M} + \text{H}]^+$ at m/z 968. ^1H NMR: $\delta(\text{ppm})$ 7.61–7.48 (30H, m, Ph–Sb), 7.21 (2H, m, Ph–Pd), 6.81 (3H, m, Ph–Pd). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta(\text{ppm})$ 140.2, 136.8, 134.8, 131.8, 130.2, 129.4, 128.9, 123.5.

3.4. Reaction of triphenylantimony with $[\text{PdBr}_2]$

Triphenylantimony (0.5 g, 1.41 mmol) in diethyl ether (2 cm^3) was added to a suspension of PdBr_2 (0.125 g, 0.47 mmol) in aqueous acetone (15 cm^3). After stirring at room temperature for 3 h an orange–yellow solid was deposited, filtered, washed with diethyl ether and dried in vacuo to afford **5**. Yield 0.290 g (63% based on Pd). M.p. 175–177 °C (decomp.). IR: $\nu(\text{Pd–Br})$ 202 cm^{-1} . ^1H NMR: $\delta(\text{ppm})$ 7.42–7.77 (30H, m, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta(\text{ppm})$ 136.6, 130.5, 130.3, 129.1.

3.5. Reaction of triphenylantimony with $[\text{Na}_2\text{PdCl}_4]$

(a) *2:1 Molar equivalent reaction at room temperature.* Triphenylantimony (0.282 g, 0.8 mmol) in diethyl ether (2 cm^3) was added to a suspension of Na_2PdCl_4 (0.120 g, 0.4 mmol) in aqueous acetone (15 cm^3). After stirring at room temperature for 3 h an orange–yellow solid was deposited, filtered, washed with diethyl ether, water and ethanol and then dried in vacuo to afford a mixture of **6** and **1** in 11:1 ratio. Yield 0.20 g (55% based on *cis*- $\text{PdCl}_2(\text{SbPh}_3)_2$). M.p. 140–142 °C (decomp.). IR: $\nu(\text{Pd–Cl})$ 270 cm^{-1} . Mass spectrum: $[\text{M} - \text{Cl}]^+$ at m/z 889. ^1H NMR: $\delta(\text{ppm})$ 7.69–7.30 (30H, m, Ph), 7.0 (2H, br, Ph–Pd), 6.62 (3H, br, Ph–Pd).

(b) *2:1 Molar equivalent reaction in refluxing aqueous acetone–diethyl ether.* Triphenylantimony (0.350 g, 1.0 mmol) in diethyl ether (2 cm^3) was added to a suspension of Na_2PdCl_4 (0.150 g, 0.51 mmol) in aqueous acetone (15 cm^3). After refluxing for 3 h an orange–yellow solid was deposited, filtered, washed with diethyl ether, water and ethanol and then dried in vacuo to afford a mixture of **6** and **1** in 33.3:1 ratio. Yield 0.320 g (68% based on *cis*- $\text{PdCl}_2(\text{SbPh}_3)_2$). Anal. Found: C, 49.1; H, 3.5; Cl, 7.9. $\text{C}_{36}\text{H}_{30}\text{Cl}_2\text{PdSb}_2$ Calc.: C, 48.9; H, 3.4; Cl, 8.0%. M.p. 140–142 °C (decomp.). IR: $\nu(\text{Pd–Cl})$ 270 cm^{-1} . Mass spectrum: $[\text{M} - \text{Cl}]^+$ at m/z 889. ^1H NMR: $\delta(\text{ppm})$ 7.72–7.36 (30H, m, Ph), 7.11–7.02 (2H, m, Ph–Pd), 6.75–6.66 (3H, m, Ph–Pd).

(c) *3:1 Molar equivalent reaction at room temperature.* Triphenylantimony (0.180 g, 0.51 mmol) in diethyl ether (1 cm^3) was added to a suspension of Na_2PdCl_4 (0.050 g, 0.17 mmol) in aqueous acetone (5 cm^3). After stirring for 3 h an orange–yellow solid was deposited, filtered, washed with diethyl ether, water and ethanol and then dried in vacuo to afford a mixture of **6** and **1** in 3:2 ratio. Yield 0.085 g (57% based on *cis*- $\text{PdCl}_2(\text{SbPh}_3)_2$). M.p. 170–172 °C (decomp. > 145 °C).

IR: $\nu(\text{Pd}-\text{Cl})$ 270, 210 cm^{-1} . Mass spectrum: $[\text{M}-\text{Cl}]^+$ at m/z 889. ^1H NMR: $\delta(\text{ppm})$ 7.66–7.17 (30H, m, Ph), 6.91–6.89 (2H, m, Ph–Pd), 6.55–6.48 (3H, m, Ph–Pd).

4. Crystal data

(a) $\text{C}_{42}\text{H}_{35}\text{ClPdSb}_2$ (**1**), $M = 925.05$, monoclinic, space group $C2/c$, $a = 16.561(2)$, $b = 11.166(2)$, $c = 19.942(3)$ Å, $\beta = 94.80(1)^\circ$, $U = 3674.7(10)$ Å³, $Z = 4$, $\mu = 2.045 \text{ mm}^{-1}$, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $F(000) = 1808$, $D_c = 1.672 \text{ Mg m}^{-3}$.

A bright yellow crystal was used for data collection with approximate dimensions $0.53 \times 0.40 \times 0.04 \text{ mm}^3$, glued to the end of a thin glass fibre using epoxy resin. Intensity data were measured on a Siemens P4 diffractometer at 293(2) K using Mo K α radiation ($\lambda = 0.71073$ Å) and an ω -scan method. 3281 reflections were measured over the range $2.94^\circ < \theta < 25.00^\circ$ with $-1 \leq h \leq 19$, $-1 \leq k \leq 13$, $-23 \leq l \leq 23$. A semi-empirical absorption correction was applied to the data based on psi scans (max., min. transmission factors 0.89 and 0.62). The reflections were corrected for Lorentz and polarisation effects and merged to give 2814 independent reflections ($R_f = 0.0217$).

The structures were solved by direct methods using the program SHELXTLPC [16] and refined using the program SHELXL 93 [17] with full-matrix least-squares on

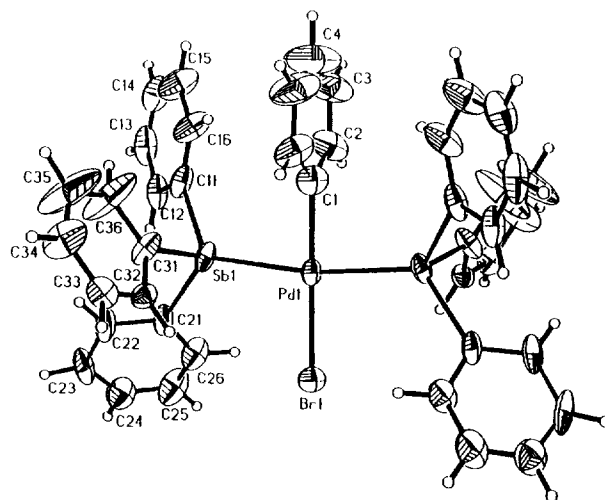


Fig. 2. Molecular structure of **2** showing the atom numbering scheme. Displacement parameters are shown at the 30% level.

F^2 . The ratio data:parameters was 7100:433. The hydrogen atoms of the phenyl rings were treated as rigid groups with C–H fixed at 0.96 Å, and a fixed isotropic displacement parameter (0.08 Å²). All other atoms were refined with anisotropic displacement parameters. Final cycles of refinement gave $R_1 = 0.0309$, $wR_2 = 0.0819$ for all data, $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 4.37P]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$. The maximum and minimum electron densities in the final ΔF map were 0.32 and -0.33 e Å^{-3} respectively.

Table 2
Fractional atomic coordinates for *trans*-PdClPh(SbPh₃)₂ (**1**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Sb(1)	3957(1)	3024(1)	1485(1)	54(1)
Pd(1)	5000	3197(1)	2500	51(1)
Cl(1)	5000	5322(2)	2500	83(1)
C(1)	5000	1391(6)	2500	61(2)
C(2)	4531(3)	747(5)	2919(3)	78(2)
C(3)	4535(5)	−487(6)	2900(4)	112(3)
C(4)	5000	−1094(10)	2500	132(6)
C(11)	3063(3)	1649(4)	1459(3)	60(1)
C(12)	3297(3)	463(5)	1512(3)	71(2)
C(13)	2718(4)	−420(5)	1524(3)	87(2)
C(14)	1919(4)	−146(7)	1485(3)	92(2)
C(15)	1678(4)	1012(7)	1418(4)	98(2)
C(16)	2246(3)	1920(5)	1406(3)	76(2)
C(21)	3196(3)	4493(4)	1187(2)	56(1)
C(22)	3012(3)	5324(5)	1664(3)	66(1)
C(23)	2488(3)	6255(5)	1497(3)	80(2)
C(24)	2147(4)	6378(6)	857(4)	87(2)
C(25)	2325(3)	5560(5)	386(3)	82(2)
C(26)	2851(3)	4616(5)	544(3)	70(1)
C(31)	4523(3)	2680(4)	583(3)	61(1)
C(32)	4353(5)	1690(6)	191(4)	104(2)
C(33)	4748(6)	1489(7)	−363(4)	127(3)
C(34)	5298(5)	2250(7)	−567(4)	102(2)
C(35)	5472(4)	3248(7)	−193(4)	97(2)
C(36)	5086(3)	3460(5)	383(3)	76(2)

Table 3
Fractional atomic coordinates for *trans*-PdBrPh(SbPh₃)₂ (**2**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Sb(1)	3952(1)	3004(1)	1499(1)	51(1)
Pd(1)	5000	3196(1)	2500	46(1)
Br(1)	5000	5445(1)	2500	61(1)
C(11)	3082(4)	1585(10)	1465(4)	64(2)
C(12)	2249(4)	1913(11)	1395(4)	69(3)
C(13)	1694(5)	958(14)	1404(5)	89(4)
C(14)	1937(6)	−225(14)	1480(6)	96(4)
C(15)	2740(6)	−485(12)	1531(7)	112(5)
C(16)	3305(6)	402(11)	1532(6)	93(4)
C(21)	3185(4)	4466(9)	1187(4)	58(2)
C(22)	2856(5)	4587(11)	533(4)	74(3)
C(23)	2294(5)	5625(12)	395(5)	86(4)
C(24)	2124(7)	6356(12)	921(7)	94(3)
C(25)	2438(6)	6204(13)	1533(7)	106(4)
C(26)	2980(5)	5319(10)	1659(5)	79(3)
C(31)	4529(4)	2672(9)	590(4)	62(2)
C(32)	5083(4)	3472(8)	402(4)	54(2)
C(33)	5479(5)	3268(9)	−187(5)	65(2)
C(34)	5317(7)	2282(12)	−556(7)	107(4)
C(35)	4782(12)	1488(16)	−369(9)	214(12)
C(36)	4376(10)	1667(15)	200(8)	181(10)
C(1)	5000	1361(13)	2500	81(5)
C(2)	4533(6)	707(11)	2910(8)	105(4)
C(3)	4540(10)	−524(14)	2899(13)	166(10)
C(4)	5000	−1103(29)	2500	256(33)

The geometry of the molecule is shown in Fig. 1. Selected bond distances and bond angles are listed in Table 1. Atom coordinates are listed in Table 2. A complete list of bond lengths and angles and a table of anisotropic displacement parameters have been deposited at the Cambridge Crystallographic Data Centre.

(b) $C_{42}H_{35}BrPdSb_2$ (**2**), $M = 969.51$, monoclinic, space group $C2/c$, $a = 16.641(3)$, $b = 11.080(1)$, $c = 19.814(2)$ Å, $\beta = 94.63(2)^\circ$, $U = 3641.4(8)$ Å³, $Z = 4$, $\mu = 3.087$ mm⁻¹, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $F(000) = 1880$, $D_c = 1.768$ Mg m⁻³.

Conditions were as for **1** except for the following: crystal size $0.45 \times 0.42 \times 0.32$ mm³; intensity data were collected at 190 K in the range $2.96^\circ < \theta < 26^\circ$ for 4376 reflections. Absorption correction max. and min. transmission factors were 0.834 and 0.575 respectively. Final cycles of refinement gave $R_1 = 0.0509$, $wR_2 = 0.1220$ for all data, $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = 1 / [\sigma^2(F_o^2) + (0.031P)^2 + 51.44P]$ and $P = [\max(F_o^2, 0) + 2F_c^2] / 3$. The maximum and minimum electron densities in the final ΔF map were 1.66 and -2.28 e Å⁻³ respectively.

The geometry of the molecule is shown in Fig. 2. Selected bond lengths and angles are given in Table 1. Atom coordinates are listed in Table 3.

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