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Metal-mediated couplings of a diphosphastibolyl ring anion, $[1,4,2\text{-}P_2SbC_2Bu^t_2]^-$: synthesis and characterisation of novel antimony-containing cage compounds

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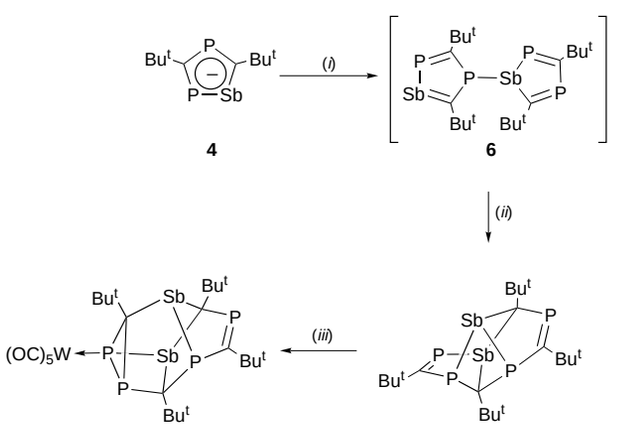
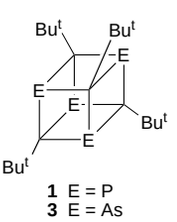
Two equivalents of the diphosphastibolyl ring anion, $[1,4,2\text{-}P_2SbC_2Bu^t_2]^-$ reacted with $FeCl_3$ to produce an antimony-containing cage compound, $P_4Sb_2C_4Bu^t_4$, *via* an oxidative coupling mechanism. This cage underwent an intramolecular rearrangement reaction when treated with $[W(CO)_5(thf)]$ (thf = tetrahydrofuran) to produce the complex $[\{W(CO)_5\}P_4Sb_2C_4Bu^t_4]$, which X-ray crystallography shows to contain a three-membered PPC 'diphosphirane' ring. Treatment of *cis*-$[PtCl_2(PEt_3)_2]$ with 1 equivalent of $[1,4,2\text{-}P_2SbC_2Bu^t_2]^-$ yielded the first example of a complex, *trans*-$[PtCl(PEt_3)_2(\eta^1\text{-}P_2SbC_2Bu^t_2)]$, containing a solely η^1-co-ordinated diphosphastibolyl ring. The crystal structure of this compound shows the heterocyclic ring to retain its aromaticity after co-ordination. Treatment of *cis*-$[PtCl_2(PEt_3)_2]$ with 2 equivalents of $[1,4,2\text{-}P_2SbC_2Bu^t_2]^-$ initiated a ring-coupling reaction at the metal to give the novel cage complex *cis*-$[Pt(PEt_3)_2(\eta^2\text{-}P_4Sb_2C_4Bu^t_4]$. The molecular structure of the cage shows it to contain a highly strained, dianionic ligand, $[P_4Sb_2C_4Bu^t_4]^{2-}$, which chelates the platinum through antimony and phosphorus atoms. Unusual features in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of the complex are described.

The study of organophosphorus cage systems is the subject of considerable current interest as a consequence of the structural similarities these compounds show to hydrocarbon cages.[1] One of the most common synthetic routes to organophosphorus cages, *e.g.* **1**,[2] is *via* the thermal or metal-mediated oligomerisation of phosphaalkynes (P≡CR). Other routes include the oxidative coupling of polyphospholyl ring anions,[3] an example of which is the reaction of a 1:1 mixture of $[1,2,4\text{-}P_3C_2Bu^t_2]^-$ and $[1,3\text{-}P_2C_3Bu^t_3]^-$ with $FeCl_3$ to give **2**.[4] In contrast to organophosphorus cages, those substituted with the heavier Group 15 elements remain almost non-existent due to the relative instability of suitable heteroalkyne and polyheterolyl precursors. A tetraarsacubane compound, **3**, has, however, been reported as arising from the tetramerisation of an *in situ* generated arsaalkyne, $As{\equiv}CBu^t$.[5]

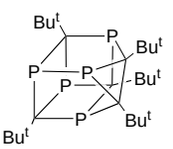
Our interest in the low co-ordination chemistry of the heavier Group 15 elements has led to the development of the diphosphastibolyl ring anion $[1,4,2\text{-}P_2SbC_2Bu^t_2]^-$ **4**.[6] In previous work with this heterocycle we have prepared a range of organometallic complexes in which **4** acts as either an η^5 or a mixed $\eta^5:\eta^1$ ligand, *e.g.* $[Rh(\eta^5\text{-}P_2SbC_2Bu^t_2)(\eta^4\text{-}C_8H_{12})]$[7] and $[Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_2SbC_2Bu^t_2)\{W(CO)_5\}]$[8] respectively. We have also identified **4** as a potential building block in the formation of antimony-containing cage compounds. To this end we have made a preliminary report of the oxidative coupling of two equivalents of **4** with $FeCl_3$ to give such a cage, **5**, which shows intermolecular interactions in the solid state.[9] Herein we report full synthetic details for **5** and the results of a metal-mediated intramolecular rearrangement it undergoes. In addition, the coupling of 2 equivalents of **4** at a platinum centre, and the formation of the first complex in which **4** acts solely as an η^1 ligand are described.



Scheme 1 (*i*) $FeCl_3$, 1,2-dimethoxyethene, 18 h; (*ii*) [4+2] cycloaddition; (*iii*) $[W(CO)_5(thf)]$, tetrahydrofuran (thf), 18 h



1 E = P
3 E = As



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Results and Discussion

As reported in a preliminary communication,[9] treatment of 1 equivalent of $[Li(tmen)_2][1,4,2\text{-}P_2SbC_2Bu^t_2]$ (tmen = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine) with $FeCl_3$ leads to the formation of the air- and moisture-stable cage compound $P_4Sb_2C_4Bu^t_4$ **5** in good yield (65%) after chromatographic work-up (Scheme 1). The mechanism for the formation of **5** presumably involves an initial coupling reaction to give the intermediate **6**, which then undergoes a [4+2] cycloaddition reaction affording **5**. Interestingly, this reaction appears to be completely specific for the formation of the observed isomer, despite the possibility of numerous other isomers obtainable from the postulated reaction mechanism. A discussion of the crystal structure and solution NMR data for **5** can be found in the previous com-

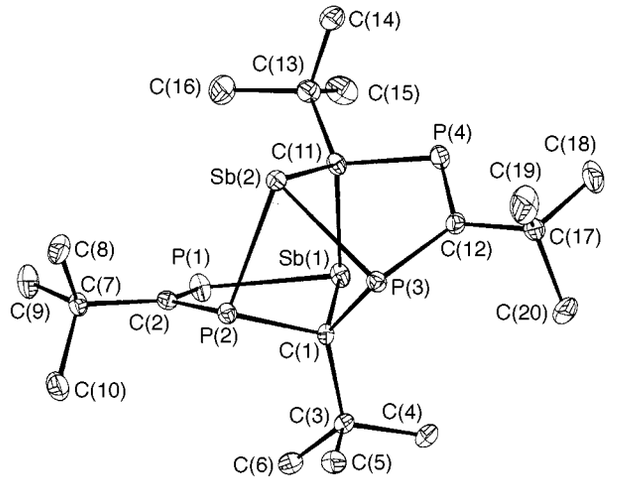


Fig. 1 Molecular structure of compound **5**[9]

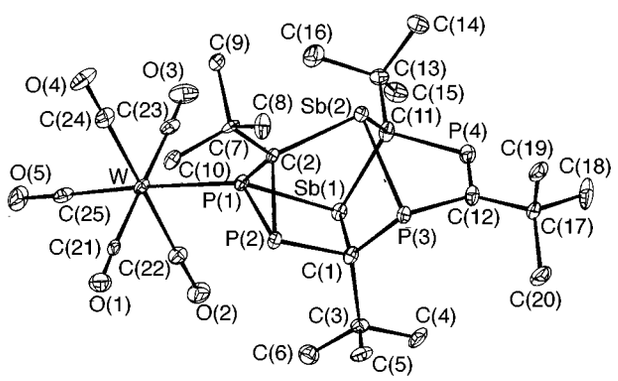


Fig. 2 Molecular structure of compound **7**

Table 1 Selected intramolecular distances (Å) and angles (°) for compound **7** with estimated standard deviations (e.s.d.s) in parentheses

W–C(25)	1.998(9)	W–C(24)	2.034(10)
W–C(21)	2.038(8)	W–C(23)	2.048(9)
W–C(22)	2.061(9)	W–P(1)	2.526(2)
Sb(1)–C(11)	2.169(9)	Sb(1)–C(1)	2.220(7)
Sb(1)–P(1)	2.531(2)	Sb(2)–C(2)	2.187(7)
Sb(2)–C(11)	2.206(7)	Sb(2)–P(3)	2.494(2)
P(1)–C(2)	1.867(7)	P(1)–P(2)	2.220(3)
P(2)–C(2)	1.876(8)	P(2)–C(1)	1.900(7)
P(3)–C(12)	1.855(7)	P(3)–C(1)	1.886(8)
P(4)–C(12)	1.708(8)	P(4)–C(11)	1.869(8)
C(25)–W–P(1)	176.2(2)	C(24)–W–P(1)	95.1(2)
C(21)–W–P(1)	88.2(2)	C(23)–W–P(1)	91.1(2)
C(22)–W–P(1)	86.1(2)	C(11)–Sb(1)–C(1)	93.0(3)
C(11)–Sb(1)–P(1)	95.5(2)	C(1)–Sb(1)–P(1)	79.9(2)
C(2)–Sb(2)–C(11)	100.2(3)	C(2)–Sb(2)–P(3)	88.1(2)
C(11)–Sb(2)–P(3)	84.5(2)	C(2)–P(1)–P(2)	53.8(2)
C(2)–P(1)–W	138.1(2)	P(2)–P(1)–W	128.51(10)
C(2)–P(1)–Sb(1)	97.9(2)	P(2)–P(1)–Sb(1)	83.51(8)
W–P(1)–Sb(1)	123.69(8)	C(2)–P(2)–C(1)	101.1(3)
C(2)–P(2)–P(1)	53.4(2)	C(1)–P(2)–P(1)	95.7(2)
C(12)–P(3)–C(1)	107.4(3)	C(12)–P(3)–Sb(2)	90.8(3)
C(1)–P(3)–Sb(2)	93.9(2)	C(12)–P(4)–C(11)	104.6(3)
C(3)–C(1)–P(3)	115.9(5)	C(3)–C(1)–P(2)	108.9(5)
P(3)–C(1)–P(2)	103.9(4)	C(3)–C(1)–Sb(1)	111.5(5)
P(3)–C(1)–Sb(1)	114.5(4)	P(2)–C(1)–Sb(1)	100.4(3)
C(7)–C(2)–P(1)	120.1(5)	C(7)–C(2)–P(2)	115.2(5)
P(1)–C(2)–P(2)	72.8(3)	C(7)–C(2)–Sb(2)	112.0(5)
P(1)–C(2)–Sb(2)	117.5(3)	P(2)–C(2)–Sb(2)	113.7(3)
C(13)–C(11)–P(4)	110.7(5)	C(13)–C(11)–Sb(1)	114.9(5)
P(4)–C(11)–Sb(1)	105.6(4)	C(13)–C(11)–Sb(2)	114.3(5)
P(4)–C(11)–Sb(2)	104.3(3)	Sb(1)–C(11)–Sb(2)	106.1(3)
C(17)–C(12)–P(4)	120.4(6)	C(17)–C(12)–P(3)	117.2(5)
P(4)–C(12)–P(3)	121.8(4)		

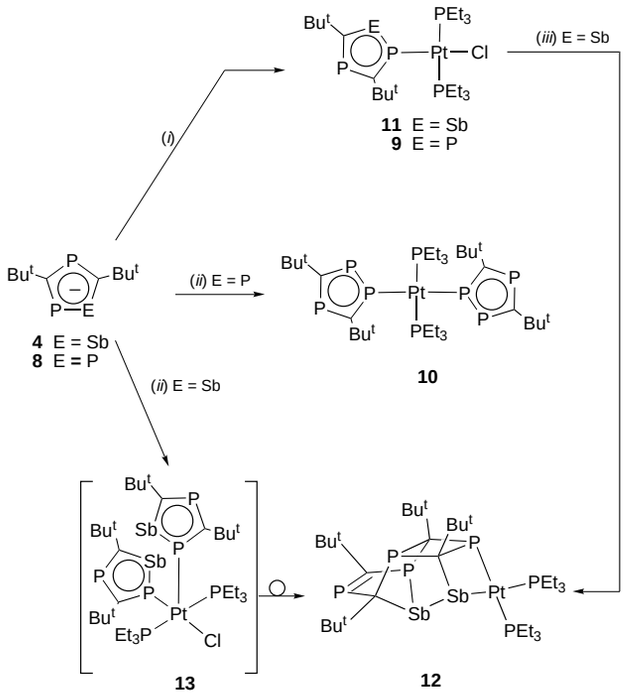
munication,[9] whereas full details of its synthesis are presented herein. The molecular structure of **5** is reproduced here (Fig. 1) for purposes of comparison.

Compound **5** offers many potential sites for metal co-ordination, either through η^1 co-ordination to the lone pairs of P and Sb, or η^2 co-ordination to its P–C double bonds. We have carried out a range of reactions to examine these possibilities. Surprisingly, treatment of **5** with an excess of $[W(CO)_5(thf)]$ did not lead to a simple adduct, but instead gave the complex **7** in low yield (9%) after column chromatography. Efforts to determine the outcome of the majority of **5** in the reaction product proved unsuccessful. It seems likely that the mechanism for the formation of **7** involves initial co-ordination of **5** to a $W(CO)_5$ fragment through P(1) (Fig. 1). An intramolecular rearrangement reaction then follows which involves cleavage of the Sb(2)–P(2) bond in **5**, and the formation of bonds between P(1) and P(2) and Sb(2) and C(2). This mechanism involves the formation of a three-membered PPC 'diphosphirane' ring at the expense of a four-membered P_2SbC ring. At first sight this may seem surprising, however such rings are a common, and apparently stable, structural motif in organophosphorus cage compounds, *e.g.* tetraphosphabishomoprismanes.[10] All attempts to co-ordinate further $W(CO)_5$ fragments to **7** met with failure due to the steric inaccessibility of its unco-ordinated heterocentres. In addition, attempts to synthesize other transition-metal adducts of **5** using $[Pt(PPh_3)_2(C_2H_4)]$, $[\{RhCl(C_8H_{12})\}_2]$ and $[\{PtCl_2(PEt_3)\}_2]$ resulted in decomposition of the cage to intractable mixtures of products.

The ^{31}P-$\{^1H\}$ NMR spectrum for complex **7** supports its proposed structure and is pseudo-first order exhibiting an ABMX spin system, with one signal to low field (δ 277.6) assigned to the unsaturated phosphorus atom and three others to high field. The resonances for P(1) and P(2) (see Fig. 2 for labelling scheme) exhibit a $^1J_{PP}$ value of 107.2 Hz which is in the expected range for diphosphirane rings.[10] Additionally, the signal for P(1) shows tungsten satellites with a $^1J_{WP}$ value of 141.3 Hz. The ^1H NMR spectrum of this complex indicates the presence of four inequivalent tertiary butyl groups, one of which is broadened considerably. This broad resonance has been attributed to the C(7)–C(10) tertiary butyl group as its free rotation is restricted by the proximity of the $W(CO)_5$ fragment. The FAB mass spectrum of **7** shows the correct molecular ion with the expected isotopic distribution and breakdown pattern. Infrared spectroscopy has confirmed the presence of a bound $W(CO)_5$ fragment.

The molecular structure of **7** is depicted in Fig. 2 (Table 1) and reveals a cage structure with a $W(CO)_5$ fragment co-ordinated to the P(1) centre, as predicted in the solution state. All bond lengths within the cage framework are normal for single-bonded interactions except P(4)–C(12) [1.708(8) Å] which is consistent with a localised P–C double bond. The angles and bond lengths within the PPC three-membered ring are similar to those reported in a related tetraphosphabishomoprismane complex, $[(P_4C_4Bu^t_4)\{W(CO)_5\}_2]$.[10] Unlike its precursor, **5**, an examination of the cell packing diagram of **7** did not reveal any intermolecular contacts between heteroatoms.

In related work we have examined the reaction of 1 and 2 equivalents of compound **4** with *cis*-$[PtCl_2(PEt_3)_2]$. This was prompted by the previous work of Nixon and co-workers,[11,12] who have carried out the analogous reactions with the related triphospholyl anion **8** to give complexes **9** and **10** (Scheme 2) in which **8** is η^1-bonded to the platinum centre and retains its aromaticity. Treatment of *cis*-$[PtCl_2(PEt_3)_2]$ with 1 equivalent of $[Li(tmen)_2][1,4,2\text{-}P_2SbC_2Bu^t_2]$ leads to the formation of the expected η^1-ligated diphosphastibolyl complex **11** in moderate yield (15%) after recrystallisation from diethyl ether. Unfortunately ^{31}P NMR studies revealed that **11** (50%) was contaminated with its triphospholyl counterpart, **9** (50%). This impurity is a result of the cosynthesis of the triphospholyl anion **8** (25%), in the preparation of the diphosphastibolyl



Scheme 2 (*i*) *cis*-$[PtCl_2(PEt_3)_2]$, thf–CH_2Cl_2, 18 h; (*ii*) ½ *cis*-$[PtCl_2(PEt_3)_2]$, thf–CH_2Cl_2, 1 h; (*iii*) $[P_2SbC_2Bu^t_2]^-$, thf, 1 h

precursor **4** (75%), the cocrystallised mixture being inseparable.[6] Rigorous attempts to separate **11** and **9** by fractional crystallisation met with failure due to their persistent cocrystallisation (see below).

The ^{31}P-{^1H} NMR data for compound **11** represent an AMX_2 pattern with ^{195}Pt satellites on all signals. The two low-field signals (P_A, δ 268, P_M 153) have a characteristic two-bond mutual coupling (40.5 Hz) and are in the expected region for delocalised P–C double bonds. Significant broadening of the P_M signal suggests this arises from the phosphorus adjacent to the quadrupolar Sb. Indeed, the J_{PtP_M} coupling (2468 Hz) on this signal suggests a one-bond interaction as would be expected with this less-hindered phosphorus centre. The magnitude of this coupling is indicative of a phosphine ligand *trans* to Cl in a square-planar platinum(II) complex[13] and, thus, suggests the aromatic nature of the ring in **11**. If this ring did not retain its aromaticity and instead possessed a saturated phosphido centre σ bonded to platinum (and localised Sb–C and P_A–C double bonds) this coupling constant would be much lower. An interesting difference in the solution-state behaviour of **9** and **11** is that **9** is fluxional at room temperature due to a rapid exchange in platinum complexation between the two adjacent phosphorus centres.[11] Compound **11** shows no such dynamic behaviour which suggests that Pt–P co-ordination is preferred over Pt–Sb in this complex.

The molecular structure of compound **11** is depicted in Fig. 3 (Table 2) and represents the first structural characterisation of a complex containing a solely η^1-bonded diphosphastibolyl ring anion. During refinement it was found that the site labelled Sb(1) is partially occupied by phosphorus (50%), whilst P(1) and P(2) have 100% phosphorus occupancies. This site disorder is consistent with the cocrystallisation of **11** and **9** and is in line with the NMR spectrum of the product mixture. Unfortunately any discussion of the bond lengths and angles within the heterocyclic ring is precluded by the observed disorder. It is clear, however, that the ring is aromatic as it is perfectly flat, lying on a crystallographic mirror plane with Pt(1) and Cl(1). The co-ordination environment of Pt(1) is distorted square planar and the bond lengths to P(3) and Cl(1) are in the normal range.

In contrast to the reaction giving compound **11**, treatment of *cis*-$[PtCl_2(PEt_3)_2]$ with 2 equivalents of $[Li(tmen)_2][1,4,2\text{-}P_2SbC_2Bu^t_2]$ did not lead to the diphosphastibolyl analogue of **10**, but instead to a ring-coupling reaction and the formation of the novel platinum(II) complex **12**, in moderate yield (27%) after recrystallisation from dichloromethane. In this case there was no evidence for the contamination of **12** with any similar product derived from the presence of **8** in the precursor **4**. Presumably, this indicates that a coupling reaction between **4** and **8** at a platinum centre will not occur. Although **12** is thermally stable in the solid state it has a half-life of only 8 h in solution at room temperature. This is most likely due to the strained nature of this species (see below).

Compound **12** can be thought of as containing a platinum(II) centre with two *cis*-PEt_3 ligands. The remaining two co-ordination sites are taken up by a chelating, dianionic ligand that is derived from the coupling of two molecules of **4**. With regard to a mechanism for the formation of **12**, it seems plausible that in the initial stages of the reaction the 1 : 1 complex **11** is formed. This then reacts with another equivalent of **4** through a five-co-ordinate intermediate **13**, as is common in nucleophilic displacement reactions at square-planar

Table 2 Selected intramolecular distances (Å) and angles (°) for the cocrystallised mixture of compounds **11** and **9** with e.s.d.s in parentheses

Pt(1)–P(1)	2.253(2)	Pt(1)–P(3)	2.3246(12)
Pt(1)–Cl(1)	2.349(2)	Sb(1)–C(2)	1.987(7)
Sb(1)–P(1)	2.327(2)	P(1)–C(1)	1.730(6)
P(2)–C(2)	1.694(7)	P(2)–C(1)	1.753(6)
P(3)–C(9)	1.822(5)	P(3)–C(11)	1.823(5)
P(3)–C(13)	1.827(5)	C(1)–C(3)	1.532(9)
C(2)–C(6)	1.554(10)	C(3)–C(5)	1.506(7)
C(3)–C(4)	1.517(10)	C(6)–C(7)	1.498(7)
C(6)–C(8)	1.518(11)	C(9)–C(10)	1.525(7)
C(11)–C(12)	1.526(8)	C(13)–C(14)	1.515(8)
P(1)–Pt(1)–P(3)	94.04(3)	P(3′)–Pt(1)–P(3)	168.76(6)
P(1)–Pt(1)–Cl(1)	176.52(6)	P(3)–Pt(1)–Cl(1)	85.73(3)
C(2)–Sb(1)–P(1)	85.9(2)	C(1)–P(1)–Pt(1)	132.6(2)
C(1)–P(1)–Sb(1)	108.3(2)	Pt(1)–P(1)–Sb(1)	119.07(8)
C(2)–P(2)–C(1)	105.8(3)	C(9)–P(3)–C(11)	105.7(2)
C(9)–P(3)–C(13)	105.2(2)	C(11)–P(3)–C(13)	102.7(2)
C(9)–P(3)–Pt(1)	118.9(2)	C(11)–P(3)–Pt(1)	114.1(2)
C(13)–P(3)–Pt(1)	108.6(2)	C(3)–C(1)–P(1)	123.9(5)
C(3)–C(1)–P(2)	120.9(5)	P(1)–C(1)–P(2)	115.1(4)
C(6)–C(2)–P(2)	120.8(5)	C(6)–C(2)–Sb(1)	114.4(5)
P(2)–C(2)–Sb(1)	124.8(4)	C(5′)–C(3)–C(5)	108.9(8)
C(5)–C(3)–C(4)	107.6(4)	C(5)–C(3)–C(1)	110.3(4)
C(4)–C(3)–C(1)	112.0(6)	C(7′)–C(6)–C(7)	112.3(9)
C(7)–C(6)–C(8)	106.4(5)	C(7)–C(6)–C(2)	109.1(4)
C(8)–C(6)–C(2)	113.6(7)	C(10)–C(9)–P(3)	116.3(4)
C(12)–C(11)–P(3)	114.8(4)	C(14)–C(13)–P(3)	114.1(4)

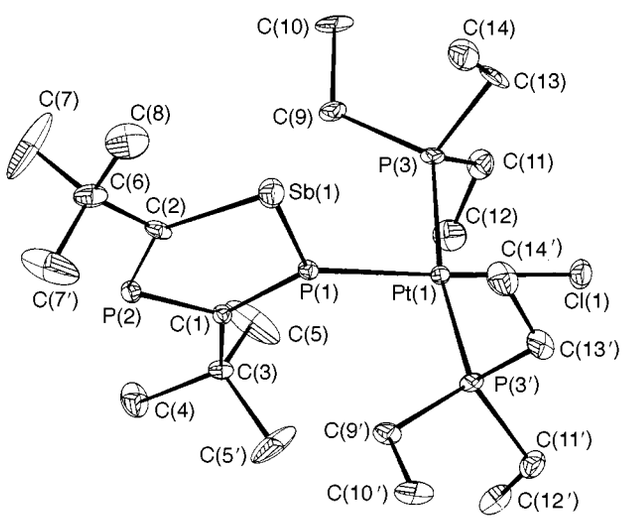


Fig. 3 Molecular structure of the cocrystallised mixture of compounds **11** and **9** (atom labels represent **11**)

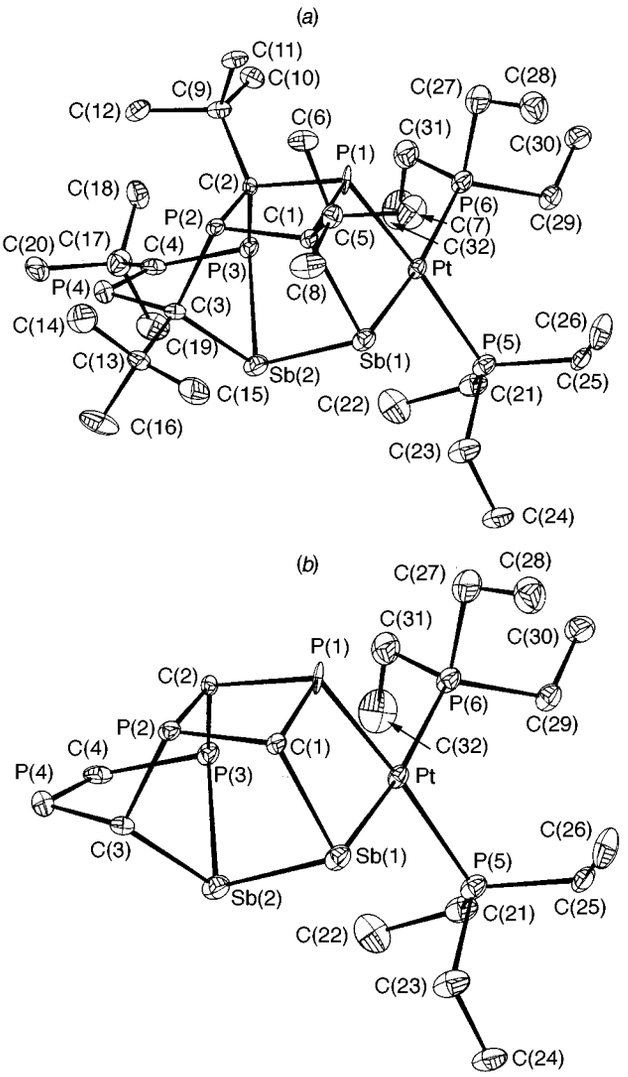


Fig. 4 (*a*) Molecular structure of compound **12**; (*b*) with tertiary butyl groups omitted for clarity

platinum(II) centres. The close proximity of two heterocycles in this intermediate could force a coupling reaction to occur prior to the displacement of the chloride ligand. It also seems that at some stage in this mechanism the platinum centre has inserted into a Sb–P bond to yield the observed product. To confirm that the ring-coupling reaction did not occur prior to platinum complexation the reaction was followed by variable-temperature ^{31}P-{^{1}H} NMR spectroscopy. At −100 °C the 1:1 complex **11** readily formed but did not react further until the mixture was warmed to −70 °C whereupon the signals due to **11** faded over a 10 min period at the expense of those due to **12** which was being formed at this temperature. It is noteworthy that no intermediate species was identified in this experiment. As a final confirmation that the ring-coupling reaction was metal mediated, complex **11** was treated with 1 equivalent of [Li(tmen)$_2$][1,4,2-$P_2SbC_2Bu^t_2$] to form **12** in *ca.* 30% yield after work-up.

The solution-state ^{31}P-{^{1}H} NMR spectrum of compound **12** is unusual in that the six phosphorus resonances are divided into two discrete spin systems, both first order. The signals for P(2), P(3) and P(4) (see Fig. 4 for labelling scheme) are in an AMX spin system with one signal to low field for P(4) and the signals for P(2) and P(3) to high field. The resonances for P(1), P(5) and P(6) all appear to high field in an AMX spin system, each showing characteristic platinum satellites. The absence of an interaction between these two sets of nuclei can be attributed to the fact that P(1), P(2), C(1) and C(2) (Fig. 4) comprise a strained four-membered ring which should result in a high degree of p character to the bonds within this ring. Thus, according to the Karplus relationship,[14] the two-bond couplings from P(1) to P(2) and P(3) should be low, and in this case are effectively zero. Another consequence of the bonding character at P(1) is the lower than expected values for the *trans*-PP coupling between P(1) and P(5) (24.5 Hz), and a low $^{1}J_{PtP(1)}$ coupling constant (1742.8 Hz). These values could also be due to the very long P(1)–Pt distance [2.434(2) Å], which presumably arises from the strained nature of the four-membered ring comprising P(1), Pt, Sb(1) and C(1). The ^{1}H and ^{13}C NMR spectra of **12** highlight the presence of four inequivalent tertiary butyl groups and two inequivalent triethylphosphines. Mass spectral data show the molecular ion with the correct isotopic distribution and expected breakdown pattern.

Table 3 Selected intramolecular distances (Å) and angles (°) for compound **12** with e.s.d.s in parentheses

Pt–P(6)	2.315(2)	Pt–P(5)	2.331(2)
Pt–P(1)	2.434(2)	Pt–Sb(1)	2.6152(7)
Sb(1)–C(1)	2.242(8)	Sb(1)–Sb(2)	2.7681(13)
Sb(2)–C(3)	2.225(8)	Sb(2)–P(3)	2.515(3)
P(1)–C(2)	1.946(8)	P(1)–C(1)	1.950(8)
P(2)–C(1)	1.871(9)	P(2)–C(3)	1.873(10)
P(2)–C(2)	1.876(8)	P(3)–C(4)	1.847(10)
P(3)–C(2)	1.893(9)	P(4)–C(4)	1.699(9)
P(4)–C(3)	1.868(10)	P(5)–C(21)	1.803(10)
P(5)–C(23)	1.827(10)	P(5)–C(25)	1.831(9)
P(6)–C(27)	1.793(12)	P(6)–C(31)	1.810(11)
P(6)–C(29)	1.859(8)		
P(6)–Pt–P(5)	99.09(8)	P(6)–Pt–P(1)	91.29(8)
P(5)–Pt–P(1)	168.79(8)	P(6)–Pt–Sb(1)	166.10(7)
P(5)–Pt–Sb(1)	92.92(6)	P(1)–Pt–Sb(1)	76.28(6)
C(1)–Sb(1)–Pt	87.6(2)	C(1)–Sb(1)–Sb(2)	89.5(2)
Pt–Sb(1)–Sb(2)	82.83(3)	C(3)–Sb(2)–P(3)	80.1(2)
C(3)–Sb(2)–Sb(1)	93.6(3)	P(3)–Sb(2)–Sb(1)	101.03(7)
C(2)–P(1)–C(1)	83.0(4)	C(2)–P(1)–Pt	107.8(3)
C(1)–P(1)–Pt	100.0(3)	C(1)–P(2)–C(3)	113.0(4)
C(1)–P(2)–C(2)	87.1(4)	C(3)–P(2)–C(2)	101.2(4)
C(4)–P(3)–C(2)	102.3(4)	C(4)–P(3)–Sb(2)	86.2(3)
C(2)–P(3)–Sb(2)	98.9(3)	C(4)–P(4)–C(3)	103.2(4)
C(5)–C(1)–P(2)	119.6(5)	C(5)–C(1)–P(1)	115.4(6)
P(2)–C(1)–P(1)	94.0(4)	C(5)–C(1)–Sb(1)	110.9(6)
P(2)–C(1)–Sb(1)	117.2(4)	P(1)–C(1)–Sb(1)	96.0(3)
C(9)–C(2)–P(2)	113.2(5)	C(9)–C(2)–P(3)	113.7(6)
P(2)–C(2)–P(3)	114.9(5)	C(9)–C(2)–P(1)	110.6(6)
P(2)–C(2)–P(1)	94.0(4)	P(3)–C(2)–P(1)	108.6(4)
C(13)–C(3)–P(4)	107.5(6)	C(13)–C(3)–P(2)	114.8(7)
P(4)–C(3)–P(2)	111.2(5)	C(13)–C(3)–Sb(2)	114.5(6)
P(4)–C(3)–Sb(2)	100.7(4)	P(2)–C(3)–Sb(2)	107.3(4)
C(17)–C(4)–P(4)	121.6(7)	C(17)–C(4)–P(3)	118.8(7)
P(4)–C(4)–P(3)	119.4(6)		

The molecular structure of compound **12** (Fig. 4, Table 3) also contains one dichloromethane molecule of crystallisation per molecule of **12** though this is not included in the figure. The structure highlights a dianionic $[P_4Sb_2C_4Bu^t_4]^{2-}$ ligand chelating a distorted square-planar platinum centre [P(1)–Pt–Sb(1) 76.28(6)°]. The bond length from Pt to P(1) [2.434(2) Å] is longer than would normally be expected [*cf.* P(6)–Pt 2.315(2), P(5)–Pt 2.331(2) Å] and probably gives rise to the small $^{1}J_{PtP(1)}$ coupling, as already mentioned. A survey of the Cambridge Crystallographic Database revealed only three compounds containing a Pt–Sb bond so comparisons are difficult. The Pt–Sb(1) distance of 2.6152(7) Å is, however, close to those reported, *e.g.* [$Pt^{II}(\eta^4$-$C_4Me_4)Cl_2(SbPh_3)$] 2.591 Å.[15] All the bond lengths within the heterocage fragment reflect single-bonded interactions except for P(4)–C(4) [1.699(9) Å] which is in the normal region for P–C double bonds. The structure also contains two strained four-membered rings [P(1)–C(2)–P(2)–C(1) and P(1)–Pt–Sb(1)–C(1)] which most likely give rise to the low thermal stability of **12** in solution and its peculiar ^{31}P NMR spectrum.

Conclusion

This study highlights the versatility of the diphosphastibolyl ring anion **4**, as a building block in the metal-mediated synthesis of antimony-containing cage compounds. The potential for the use of such cages as ligands has been explored, and it has been found that metal co-ordination can initiate rearrangement reactions in these cages. It is noteworthy that although we have previously shown the co-ordination behaviour of **4** to be very similar to that of its triphospholyl analogue **8**, ring-coupling reactions analogous to those reported here have not been observed for **8**. We believe this is due to an enhanced reactivity of **4** relative to **8**, which should lead to its future utilisation in the synthesis of other novel organometallic cage compounds.

Experimental

General remarks

All manipulations were carried out using standard Schlenk and glove-box techniques under an atmosphere of high-purity argon or dinitrogen. The solvents tetrahydrofuran, 1,2-dimethoxyethane and hexane were distilled over Na/K alloy then freeze/thaw degassed prior to use. Dichloromethane was distilled from CaH_2 prior to use. Proton ^{13}C and ^{31}P NMR spectra were recorded on either a Bruker WM-250 or a AM 400 spectrometer in C_6D_6, [$^2H_8$]toluene or CD_2Cl_2 and were referenced to the residual ^1H resonances of the solvent used (^1H NMR), the ^{13}C resonance of the deuteriated solvent (^{13}C NMR) or to external 85% H_3PO_4 (δ 0.0, ^{31}P NMR) respectively. Mass spectra were recorded using VG 12-253 quad/ 70 eV (*ca.* 1.12×10^{-17} J) (EI/CI) or VG-autospec/ Cs^+ ions / 25 kV / 3-nitrobenzyl alcohol matrix (FAB) instruments and conditions. Microanalyses were obtained from the University of Wales, Cardiff Microanalytical Service. Melting points were determined in sealed glass capillaries under argon, and are uncorrected. The melting point for the cocrystallised mixture of **9** and **11** is included for the benefit of experimenters wishing to repeat this synthesis. The quoted approximate percentage yield for the **11** component of the cocrystallised mixture (**9** and **11**) was calculated by relating the integration of the ^1H NMR signals of each component in the mixture to the total weight yield and is calculated on the transition-metal precursor. Reproducible microanalytical data could not be obtained for compounds **11** and **7** due to cocrystallisation with the impurity **9**, and slow decomposition at room temperature respectively. The starting materials [Li(tmen)$_2$][$P_2SbC_2Bu^t_2$][6] and *cis*-[$PtCl_2$(PEt$_3$)$_2$][16] were prepared by published procedures. All other reagents were used as received.

Syntheses

$P_4Sb_2C_4Bu^t_4$ 5. A solution of [Li(tmen)$_2$][$P_2SbC_2Bu^t_2$] (1.0 g, 1.86 mmol) in dme (15 cm^3) was added to a suspension of $FeCl_3$ (0.3 g, 1.86 mmol) in dme (15 cm^3) at 233 K. The mixture was warmed to ambient temperature and stirred for 18 h. Volatiles were removed *in vacuo* and the residue was extracted in hexane. Purification by column chromatography (Kieselgel, hexane) and recrystallisation from hexane afforded compound **5** as a red microcrystalline product (0.389 g, 65%), m.p. 82 °C (decomp.). ^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) and 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), 31.8 (dd, C*C*H$_3$, $^3J_{PC}$ = 11.4, 10.0), 32.7 (dd, C*C*H$_3$, $^3J_{PC}$ = 6.0, 9.1), 36.3 (d, C*C*H$_3$, $^3J_{PC}$ = 10.4), 38.6 (d, *C*CH$_3$, $^2J_{PC}$ = 16.2), 42.1 (dd, *C*CH$_3$, $^2J_{PC}$ = 22.0, 21.0), 46.2 (dd, *C*CH$_3$, $^2J_{PC}$ = 14.9, 12.6), 47.7 (dd, *C*CH$_3$, $^2J_{PC}$ = 12.1, 14.2), 79.0 (ddd, PCP, $^1J_{PC}$ = 50, 51, $^3J_{PC}$ = 8 Hz), 90.5 (d, SbCP, $^1J_{PC}$ = 65), 212.0 (ddd, PCP, $^1J_{PC}$ = 77, 74, $^3J_{PC}$ = 10.1) and 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), $^2J(P^2P^3)$ = 137, $^2J(P^1P^2)$ = 28], 32.5 [dd, P(3), $^2J(P^2P^3)$ = 137, $^2J(P^3P^4)$ = 31], 356.5 [d, P(4), $^2J(P^3P^4)$ = 31] and 363.4 [d, P(1), $^2J(P^1P^2)$ = 28 Hz]. CI mass spectrum (70 kV): *m/z* 645 ([*M* + H]$^+$, 8), 523 ([*M* + H − Sb]$^+$, 10), 169 (Bu^{t}CPCBu^{t+}, 15) and 57 (Bu^{t+}, 100%) (Found: C, 37.19; H, 5.78. Calc. for $C_{20}H_{36}P_4Sb_2$: C, 37.26; H, 5.59%).

[{W(CO)$_5$}($P_4Sb_2C_4Bu^t_4$)] 7. A solution of compound **5** (0.15 g, 0.23 mmol) in thf (10 cm^3) was added to a solution of [W(CO)$_5$(thf)] (0.23 g, 0.58 mmol) in thf (75 cm^3) at ambient temperature and stirred for 18 h. Volatiles were removed *in vacuo* and the residue was extracted with hexane. Purification by column chromatography (Kieselgel, hexane) and recrystallisation from diethyl ether afforded **7** as pale orange crystals (0.02 g, 9%), m.p. 160 °C (decomp.). ^1H NMR (250 MHz, C_6D_6, 298 K): δ 1.13 (s), 1.15 (s), 1.47 (br), 1.65 (s) (4 × 9 H, Bu^t). ^{31}P-{^1H} NMR (101.2 MHz, C_6D_6, 298 K): δ −142.5 [d, $^1J_{PP}$ = 107.2, $^1J_{PW}$ = 141.3, P(1)], −40.3 [dd, $^1J_{PP}$ = 107.2, $^2J_{PP}$ = 48.1, P(2)], 22.3 [dd, $^2J_{PP}$ = 48.1, 19.2, P(3)] and 277.6 [d, $^2J_{PP}$ = 19.2 Hz, P(4)]. IR (Nujol) ṽ/cm^{-1} 2069.0m, 1940.0s and 1919.2s. FAB mass spectrum: *m/z* 968 (*M*$^+$, 10), 644 {[*M* − W(CO)$_5$]$^+$, 25} and 323 {[W(CO)$_5$]$^+$, 100%}.

***trans*-[PtCl(PEt$_3$)$_2$(η^1-$P_2SbC_2Bu^t_2$)] 11.** A solution of [Li(tmen)$_2$][$P_2SbC_2Bu^t_2$] (1.0 g, 1.86 mmol) in thf (15 cm^3) was added to a solution of *cis*-[$PtCl_2$(PEt$_3$)$_2$] (0.91 g, 1.86 mmol) in CH_2Cl_2–thf (5 cm^3 : 10 cm^3) at 233 K. The solution was warmed to ambient temperature and stirred for 18 h. Volatiles were removed *in vacuo* and the residue was washed with hexane (20 cm^3) and extracted into diethyl ether (10 cm^3). Cooling this solution to −30 °C yielded dark red cocrystals of **11** (*ca.* 50%) and **9** (*ca.* 50%) (containing 0.245 g of **11**, 15%), m.p. 165 °C. **11**: ^1H NMR (250 MHz, $C_6D_6CD_3$, 298 K) δ 1.63 (br, 12 H, C*H*$_2$), 1.83 (br, 18 H, CH$_2$C*H*$_3$), 1.96 (s, 9 H, Bu^t) and 1.99 (s, 9 H, Bu^t): ^{13}C-{^1H} NMR (100.6 MHz, $C_6D_6CD_3$, 298 K) δ 3.5 [d, $^2J_{PC}$ = 7.5, P(CH$_2$*C*H$_3$)$_3$], 10.1 [d, $^1J_{PC}$ = 19, $^2J_{PtC}$ = 34.7, P(*C*H$_2$CH$_3$)$_3$], 32.3 [dd, $^3J_{PC}$ = 11.1, 9.3, C(*C*H$_3$)$_3$], 32.6 [d, $^3J_{PC}$ = 13.5, C(*C*H$_3$)$_3$], 36.7 [dd, $^2J_{PC}$ = 23.2, 23.1, *C*(CH$_3$)$_3$], 40.5 [d, $^2J_{PC}$ = 21.8, *C*(CH$_3$)$_3$], 182.3 (dd, $^1J_{PC}$ = 74.1, 74.2, PCP) and 223.8 (dd, $^1J_{PC}$ = 68.4, $^2J_{PC}$ = 15.2 Hz, SbCP); ^{31}P-{^1H} NMR (101.2 MHz, $C_6D_6CD_3$, 298 K) δ 8.5 (d, $^2J_{PP}$ = 36.5 Hz, $^1J_{PtP}$ = 2372.1, PEt$_3$), 153.2 (dt, $^2J_{PP}$ = 36.5, 40.5, $^1J_{PtP}$ = 2467.9, SbPC) and 268.0 (d, $^2J_{PP}$ = 40.5, $^3J_{PtP}$ = 68.0 Hz, CPC); FAB mass spectrum, *m/z* 788 (*M*$^+$, 25), 670 (*M*$^+$ − PEt$_3$, 20), 552 (*M*$^+$ − 2PEt$_3$, 10) and 466 (*M*$^+$ − $P_2SbC_2Bu^t_2$, 100%).

***cis*-[Pt(PEt$_3$)$_2$(η^2-$P_4Sb_2C_4Bu^t_4$)]·CH_2Cl_2 12.** A solution of [Li(tmen)$_2$][$P_2SbC_2Bu^t_2$] (1.0 g, 1.86 mmol) in thf (15 cm^3) was added to a solution of *cis*-[$PtCl_2$(PEt$_3$)$_2$] (0.45 g, 0.93 mmol) in CH_2Cl_2–thf (5 cm^3 : 10 cm^3) at 233 K. The solution was warmed to ambient temperature and stirred for 1 h. Volatiles were removed *in vacuo* and the residue was extracted with hexane. Subsequent recrystallisation from CH_2Cl_2 afforded compound **12** as a dark red crystalline solid (0.285 g, 27%), m.p. 158 °C (decomp.). ^1H NMR (250 MHz, CD_2Cl_2, 298 K): δ 0.87 (br, 12 H, CH$_2$), 0.98 (br, 18 H, CH$_2$C*H*$_3$), 1.50 (s, 9 H, Bu^t), 1.53 (s, 9 H, Bu^t), 1.68 (s, 9 H, Bu^t) and 1.84 (s, 9 H, Bu^t). ^{13}C-{^1H} NMR (100.6 MHz, CD_2Cl_2, 298 K): δ 7.95 [d, $^2J_{PC}$ = 11.7, P(CH$_2$*C*H$_3$)$_3$], 8.62 [d, $^2J_{PC}$ = 10.0, P(CH$_2$*C*H$_3$)$_3$], 17.1 [d, $^1J_{PC}$ = 21.8, P(*C*H$_2$CH$_3$)$_3$], 17.8 [d, $^1J_{PC}$ = 23.7, P(*C*H$_2$CH$_3$)$_3$], 29.3 [dd, $^3J_{PC}$ = 8.1, 8.3, C(*C*H$_3$)$_3$], 29.8 [dd, $^1J_{PC}$ = 38.6, 37.4, PCP, C(1)], 30.3 [dd, $^3J_{PC}$ = 8.1, 8.2, C(*C*H$_3$)$_3$], 32.4 [ddd, $^3J_{PC}$ = 7.0, 7.5, 6.9, C(*C*H$_3$)$_3$], 33.1 [ddd, $^2J_{PC}$ = 15.9, 14.6, 14.1, *C*(CH$_3$)$_3$], 34.3 [dd, $^3J_{PC}$ = 5.6, 5.3, C(*C*H$_3$)$_3$], 36.6 [dd, $^1J_{PC}$ = 50.4, 50.2, PCP, C(3)], 39.5 [dd, $^2J_{PC}$ = 16.3, 12.6, *C*(CH$_3$)$_3$], 40.9 [dd, $^2J_{PC}$ = 15.9, 14.8, *C*(CH$_3$)$_3$], 42.6 [ddd, $^1J_{PC}$ = 153.7, 52.1, 45.6, PCP, C(2)], 43.3 [dd, $^2J_{PC}$ = 17.4, 17.3, *C*(CH$_3$)$_3$] and 98.9 [dd, $^1J_{PC}$ = 68.1, 64.5, PCP, P(4)]. ^{31}P-{^1H} NMR (101.2 MHz, CD_2Cl_2, 298 K): δ −2.5 [dd, $^2J_{PP}$ = 24.5, 17.3, $^1J_{PtP}$ = 2095.6, P(5)], −0.2 [d, $^2J_{PP}$ = 17.3, $^1J_{PtP}$ = 2606.8,

Table 4 Crystal data for $[\{W(CO)_5\}(P_4Sb_2C_4Bu^t_4)]$ **7**, the cocrystallised mixture of *trans*-$[PtCl(PEt_3)_2(\eta^1\text{-}P_2SbC_2Bu^t_2)]$ **11** and *trans*-$[PtCl(PEt_3)_2(\eta^1\text{-}P_3C_2Bu^t_2)]$ **9**, and *cis*-$[Pt(PEt_3)_2(P_4Sb_2C_4Bu^t_4)]\cdot CH_2Cl_2$ **12**

	7	**9**,**11**	**12**
Chemical formula	$C_{25}H_{36}O_5P_4Sb_2W$	$C_{22}H_{48}ClP_{4.5}PtSb_{0.5}$	$C_{33}H_{68}Cl_2P_6PtSb_2$
M	967.77	743.38	1160.18
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	*Pnma*	$P2_1/n$
a/Å	10.0720(14)	18.088(2)	10.693(4)
b/Å	11.7350(10)	13.313(2)	18.842(2)
c/Å	14.8150(6)	12.896(3)	22.7370(8)
α/°	81.27(2)		
β/°	75.820(7)		102.15(2)
γ/°	74.440(9)		
U/Å^3	1628.5(3)	3105.4(9)	4478(2)
Z	2	4	4
D_c/g cm^{-3}	1.974	1.590	1.721
μ(Mo-Kα)/cm^{-1}	53.398	52.70	46.69
DIFABS absorption correction, T_{max}, T_{min}	1.14, 0.85	1.17, 0.84	1.16, 0.89
F(000)	924	1472	2280
Reflections collected	6751	12 472	16 811
No. unique reflections	4508	2528	6590
Crystal size/mm	0.18 × 0.23 × 0.25	0.20 × 0.23 × 0.15	0.21 × 0.15 × 0.23
θ Range/°	1.81–25.11	1.94–25.08	1.83–25.03
R^a (all data)	0.0367	0.0394	0.0601
$[I>2\sigma(I)]$	0.0330	0.0301	0.0418
R'^b (all data)	0.0835	0.0633	0.0998
$[I>2\sigma(I)]$	0.0828	0.0623	0.0969

^{a} $R = \Sigma(\Delta F)/\Sigma(F_o)$. ^{b} $R' = [\Sigma w(\Delta F^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2]$, where $P = [\max(F_o^2) + 2(F_c^2)]/3$ and $a = 0.039$ for **7**, 0.035 for **9**, **11** and 0.038 for **12**.

P(6)], 7.6 [d, $^2J_{PP}$ = 24.5, $^1J_{PtP}$ = 1742.8, P(1)], 31.3 [dd, $^2J_{PP}$ = 11.9, 12.1, $^3J_{PtP}$ = 298.7, P(2)], 72.7 [d, $^2J_{PP}$ = 12.1 Hz, $^3J_{PtP}$ = 162.3, P(3)] and 270.7 [d, $^2J_{PP}$ = 11.9 Hz, P(4)]. FAB mass spectrum: *m*/*z* 1075 (M^+, 15), 957 ($[M - PEt_3]^+$, 15), 839 ($[M - 2PEt_3]^+$ 5) and 431 ($[M - C_{20}H_{36}Sb_2P_4]^+$, 100%) (Found: C, 34.90; H, 6.35. Calc. for $C_{33}H_{68}Cl_2P_6PtSb_2$: C, 34.16; H, 5.91%).

Crystallography

Crystals of compounds **7** and **12**, and cocrystals of **9** and **11**, suitable for structure determination were mounted in silicone oil. Intensity data were measured at 150(2) K on a FAST[17] area-detector diffractometer using Mo-Kα radiation (λ 0.710 69 Å). All structures were solved by heavy-atom methods (SHELXS 86[18]) and refined by least squares using the SHELXL 93[19] program. The structures were refined on F^2 using all data. Neutral-atom complex scattering factors were employed.[20] Empirical absorption corrections were carried out by the DIFABS method.[21] Crystal data, details of data collections and refinement are given in Table 4. Anisotropic thermal parameters were refined for all non-hydrogen atoms. The hydrogen atoms in all structures were included in calculated positions (riding model). During refinement of the structure of **11** and **9** a site disorder was found to exist in which the site labelled Sb(1) is partially occupied by phosphorus (50%).

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