# Preparation, properties and structures of the first series of organometallic Pt(II) and Pt(IV) complexes with stibine co-ligands

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The planar Pt(II) monomers [PtMe<sub>2</sub>(L–L)] and [(PtMe<sub>2</sub>)<sub>2</sub>(L'–L')<sub>2</sub>] dimers (L–L = R<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbR<sub>2</sub>, *o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SbMe<sub>2</sub>)<sub>2</sub>; L'–L' = R<sub>2</sub>SbCH<sub>2</sub>SbR<sub>2</sub>; R = Me or Ph) are obtained in good yield *via* reaction of [PtMe<sub>2</sub>(SMe<sub>2</sub>)<sub>2</sub>] with L–L or L'–L' in benzene. The Pt(IV) stibines, [PtMe<sub>3</sub>(L–L)I] (L–L = R<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>-SbR<sub>2</sub>, *o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SbMe<sub>2</sub>)<sub>2</sub> or 2 × SbPh<sub>3</sub>, SbMePh<sub>2</sub> or SbMe<sub>2</sub>Ph) are obtained by treatment of [PtMe<sub>3</sub>I] with L–L in chloroform. These represent the first series of stable Pt(IV) stibine complexes. All of the products have been characterised by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>195</sup>Pt NMR spectroscopy, electrospray mass spectrometry and analysis. Crystal structure determinations on [PtMe<sub>3</sub>{R<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbR<sub>2</sub>}I], [PtMe<sub>3</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SbMe<sub>2</sub>)<sub>2</sub>]I] and [PtMe<sub>3</sub>(SbPh<sub>3</sub>)<sub>2</sub>I] confirm the distorted octahedral environment at Pt, with *fac* Me groups and mutually *cis* Sb donor atoms. The Sb–Pt–Sb angle in the seven-membered chelate ring of the *o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SbMe<sub>2</sub>)<sub>2</sub> complex is *ca*. 96°, compared to <90° in the complexes with six-membered chelates. The C<sub>1</sub>-distibines R<sub>2</sub>SbCH<sub>2</sub>SbR<sub>2</sub> afford only the dinuclear [(PtMe<sub>3</sub>)<sub>2</sub>(µ-R<sub>2</sub>SbCH<sub>2</sub>SbR<sub>2</sub>)(µ-I)<sub>2</sub>] in which the stibine ligand and two I atoms bridge two Pt atoms giving an edge sharing bioctahedral geometry which has been confirmed by a crystal structure analysis. The Pt(II) species undergo oxidative addition with MeI to give the corresponding Pt(IV) species, while the Pt(IV) species reductively eliminate ethane upon thermolysis.

## Introduction

Phosphines are incorporated as co-ligands in many transition metal based homogeneous catalysts and correspondingly, the chemistry of these ligands with organometallic fragments has been investigated intensively over many years and much is known regarding the steric and electronic influences of the ligands on the metal ion and associated reaction chemistry. In contrast, with the exception of metal carbonyl species, the organometallic chemistry of transition metal stibine complexes has been much less studied.<sup>1,2</sup> Key exceptions are the very elegant work of Werner and co-workers who have demonstrated that these species promote different reaction chemistry reflecting the very different electronic properties of the stibine ligands.<sup>3-6</sup> Further,  $[Ni(CH_2C(Me)CH_2)(SbPh_3)_3]^+$  is reported to be an efficient styrene polymerisation catalyst.<sup>7</sup>

The data available on transition metal stibine complexes clearly show that these prefer low or medium oxidation state metal centres. A small number of Pt(IV) stibines of general formula *cis*-[PtCl<sub>4</sub>(distibine)] have been isolated in the solid state, but decompose immediately in solution with chlorination of the stibine and reduction of the Pt centre.<sup>8</sup> With the exception of one example from our own preliminary work in the area,<sup>9</sup> there are no Pt(IV) stibine complexes with alkyl co-ligands. There is an early report concerning the preparation of a small number of planar Pt(II) dialkyl and diaryl complexes involving SbPh<sub>3</sub> ligands, *cis*-[PtR<sub>2</sub>(SbPh<sub>3</sub>)<sub>2</sub>] (R = Me, Ph, o/m/p-C<sub>6</sub>H<sub>4</sub>Me), by treatment of [PtR<sub>2</sub>(C<sub>8</sub>H<sub>8</sub>)] with two molar equivalents of SbPh<sub>3</sub> in refluxing benzene, although no spectroscopic or structural data are included.<sup>10</sup> The photochemical activity of the purported [PtR'<sub>2</sub>(Ph<sub>2</sub>SbCH<sub>2</sub>SbPh<sub>2</sub>)] (R' = various substituted phenyl ligands) has been reported, although again the parent compounds have not been characterised either spectroscopically or structurally.<sup>11</sup>

In this paper we describe a systematic study of the coordination of the distibine ligands  $R_2Sb(CH_2)_3SbR_2$ ,  $R_2SbCH_2SbR_2$  (R = Me or Ph) and o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SbMe<sub>2</sub>)<sub>2</sub> with methyl Pt(II) and Pt(IV) reagents, including their syntheses and spectroscopic properties. Selected examples with monostibines are also prepared for comparative purposes. Crystal structures of five representative examples involving Pt(IV) are described which provide the basis for comparisons of the Pt–Sb bonding in these species.

The synthesis and reaction chemistry of Pt(II)-dimethyl and Pt(IV)-trimethyl fragments with a wide range of phosphine and arsine ligands has been studied in detail,<sup>12</sup> and hence the data on these compounds provide a useful comparison against the new stibine complexes reported here.

# **Results and discussion**

# Pt(II) Complexes

The light yellow Pt(II) dimethyl complex, [PtMe<sub>2</sub>{Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>-SbPh<sub>2</sub>}] was obtained in good yield through treatment of [PtMe<sub>2</sub>(cod)] with one molar equivalent of the distibine in toluene solution for *ca.* 12 h at room temperature. The <sup>1</sup>H NMR spectrum shows clear evidence for coordination of the distibine to the PtMe<sub>2</sub> fragment, displaying a single Pt–Me resonance with <sup>2</sup>J<sub>Pt-H</sub> 85 Hz. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum shows the  $\delta$ (Me) resonance at -3.63 ppm with <sup>1</sup>J<sub>PtC</sub> = 716 Hz, together with resonances due to the coordinated distibine. There is no

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residual cod evident in the spectra of the product, indicating clean substitution. The  ${}^{1}J_{Pt-C}$  coupling constant in the distibine complex is significantly larger than in the directly comparable  $[PtMe_2{Ph_2P(CH_2)_3PPh_2}]$  (595 Hz),<sup>13</sup> consistent with the stibine being lower in the *trans* influence series than the phosphine. The  $[PtMe_2{Ph_2Sb(CH_2)_3SbPh_2}]$  shows a single <sup>195</sup>Pt resonance at -4804 ppm. Attempts to obtain the corresponding [PtMe<sub>2</sub>(L-L)]  $(L-L = Me_2Sb(CH_2)_3SbMe_2$  or  $o-C_6H_4(CH_2SbMe_2)_2)$  by reaction of [PtMe<sub>2</sub>(cod)] and L-L in toluene at room temperature for a prolonged period (>24 h) resulted in only partial substitution of the cod. Heating the reactions led to decomposition, with the solutions turning dark brown/black. Hence, an alternative route utilising the much more labile  $[PtMe_2(SMe_2)_2]$  was employed. While reaction of [PtMe<sub>2</sub>(SMe<sub>2</sub>)<sub>2</sub>] with Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> solution produces [PtMe<sub>2</sub>{Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}] cleanly and in high yield (NMR evidence), the other distibines did not react cleanly in CH<sub>2</sub>Cl<sub>2</sub> solution. However, room temperature reaction of a benzene solution of  $[PtMe_2(SMe_2)_2]$  with distibine gives the corresponding mononuclear  $[PtMe_2(L-L)]$  (L-L =  $Me_2Sb(CH_2)_3SbMe_2$ ,  $o-C_6H_4(CH_2SbMe_2)_2$ ) or, with the short

 $C_1$  linked distibutes, the dimeric  $[(PtMe_2)_2(L'-L')_2]$   $(L'-L' = Me_2SbCH_2SbMe_2$  or  $Ph_2SbCH_2SbPh_2$ ) in high yield as light yellow solids (or in the case of  $Me_2Sb(CH_2)_3SbMe_2$ , a pale yellow oil)—Scheme 1.

The electrospray mass spectra (MeCN) show the major species to be loss of a Me group from the parent complex, [P -Me]<sup>+</sup>, in each case, providing strong supporting evidence for the monomeric and dimeric formulations respectively. Even in benzene solution slow decomposition was observed. This was most notable for [(PtMe<sub>2</sub>)<sub>2</sub>(Ph<sub>2</sub>SbCH<sub>2</sub>SbPh<sub>2</sub>)<sub>2</sub>] which undergoes decomposition quite rapidly even in the solid state, hindering analytical measurements. Spectroscopically (Table 1) these compounds are similar to  $[PtMe_2{Ph_2Sb(CH_2)_3SbPh_2}]$  above, showing similar Pt-C and Pt-H couplings within the dialkyl-Pt unit, and with the  ${}^{13}C{}^{1}H$  NMR shift for the SbMe units appearing to low frequency of Me<sub>4</sub>Si. The <sup>195</sup>Pt NMR shifts are all ca. -4800 ppm, some 400 to 500 ppm to low frequency of the Pt(IV) complexes, [PtMe<sub>3</sub>I(distibine)] below. Little platinum-195 NMR data on stibine complexes are available; however  $\delta$ <sup>(195</sup>Pt) for  $[PtCl_2{Ph_2Sb(CH_2)_3SbPh_2}]$  and  $[PtCl_2{Me_2Sb(CH_2)_3SbMe_2}]$ 



Table 1 Selected NMR spectroscopic data for Pt(II) and Pt(IV) stibine complexes

 Complex	$\delta(^{13}C{^1H}) (ppm)$	$^{1}J_{\rm PtC}/{\rm Hz}$	$\delta(^{195}\text{Pt}) \text{ (ppm)}$
Pt(II)			
$[PtMe_{2}{Ph_{2}Sb(CH_{2})_{2}SbPh_{2}}]$	-3.63 PtMe	716	-4804
$[PtMe_{2}{Me_{2}Sb(CH_{2})_{2}SbMe_{2}}]^{\alpha}$	-4.98 PtMe	b	-4722
$[PtMe_2\{o-C_6H_4(CH_2SbMe_2)_2\}]^a$	-3.85 PtMe	726	-4687
$[(PtMe_2)_2(Me_2SbCH_2SbMe_2)_2]^a$	-3.96 PtMe	711	-4802
$\mathbf{D}_{\mathbf{f}}(\mathbf{n}_{\mathbf{f}})$			
$[PtMe_3{PhSb(CH_2)_3SbPh_2}]$	-3.17 (1C) PtMe trans I	616	-4381
	5.31 (2C) PtMe trans Sb	575	
$[PtMe_3{Me_2Sb(CH_2)_3SbMe_2}]$	-6.20 (1C) PtMe trans I	628	-4491
	1.85 (2C) PtMe trans Sb	553	
$[PtMe_3{o-C_6H_4(CH_2SbMe_2)_2}]$	-6.20 (1C) PtMe trans I	611	-4384
	3.82 (2C) PtMe trans Sb	562	
$[(PtMe_3)_2(\mu-Ph_2SbCH_2SbPh_2)(\mu-I)_2]$	5.53 (2C) PtMe trans I	655	-4360
	8.27 (1C) PtMe trans Sb	684	
$[(PtMe_3)_2(\mu-Me_2SbCH_2SbMe_2)(\mu-I)_2]$	4.17 (2C) PtMe trans I	692	-4509
	12.78 (1C) PtMe trans Sb	571	
$[PtMe_3(SbPh_3)_2I]$	-3.72 (1C) PtMe trans I	606	-4380
	10.43 (2C) PtMe trans Sb	542	
[PtMe <sub>3</sub> (SbMePh <sub>2</sub> ) <sub>2</sub> I]	-5.04 (1C) PtMe trans I	611	-4419
	7.59 (2C) PtMe trans Sb	566	
$[PtMe_3(SbMe_2Ph)_2I]$	-5.87 (1C) PtMe trans I	643	-4471
	5.16 (2C) PtMe trans Sb	564	

" Spectra recorded in d6-benzene; others in CDCl3. " Pt-C coupling unclear.

are -4556 and -4553 respectively, some 250 ppm to high frequency of the Pt(II) methyl analogues in this work.<sup>14</sup>

## Pt(IV) Complexes

Reaction of [PtMe<sub>3</sub>I] with one molar equivalent of L–L in refluxing CHCl<sub>3</sub> solution affords pale yellow solutions from which the neutral, highly soluble Pt(IV) complexes [PtMe<sub>3</sub>(L–L)I] (L–L =  $R_2Sb(CH_2)_3SbR_2$ ; R = Me or Ph; o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SbMe<sub>2</sub>)<sub>2</sub> or L–L = 2 × SbPh<sub>3</sub>, SbPh<sub>2</sub>Me or SbPhMe<sub>2</sub>) and the iodo-bridged [(PtMe<sub>3</sub>I)<sub>2</sub>(R<sub>2</sub>SbCH<sub>2</sub>SbR<sub>2</sub>)] dinuclear species were obtained in high yield as air-stable powdered solids—Scheme 2.

The formation of the ligand bridged dinuclear species  $[(PtMe_3)_2(\mu-R_2SbCH_2SbR_2)(\mu-I)_2]$  is presumably a consequence of the short methylene linkage between the Sb centres, which hinders chelation. This is the product isolated even when a 1 : 1 Pt : distibute ratio is used. The related  $[(PtMe_3)_2(\mu-Ph_2PCH_2PPh_2)(\mu-I)_2]$  has been described by Puddephatt and co-workers.<sup>15</sup>

The products are extremely soluble in organic solvents and hence isolation of powdered solids required trituration of the oily materials with a small volume of cold hexane. For the Pt(IV) complexes with chelating distibines electrospray mass spectrometry (MeCN) generally shows that the only significant species in each case are [PtMe(L–L)]<sup>+</sup> and [PtMe(L–L)(MeCN)]<sup>+</sup>. However, for those complexes with either monodentate stibines or bridging distibines, the only significant fragments evident by electrospray mass spectrometry are [PtMe<sub>3</sub>(MeCN)<sub>n</sub>]<sup>+</sup> (n = 1, 2and 3), indicating easy cleavage of the Pt–Sb bonds in these systems under the MS conditions.

The NMR spectroscopic data for these, the first stable Pt(IV) stibine complexes, are summarised in Table 1. The general trends in the chemical shifts and coupling constants replicate those observed previously for phosphine and arsine derivatives.<sup>16</sup> The <sup>1</sup>H NMR spectra for these compounds each show two Pt–Me resonances consistent with the above formulations. The  ${}^{2}J_{Pt-H}$  values are in accord with the trends seen in phosphine and arsine complexes derived from [PtMe<sub>3</sub>I], with larger couplings occurring for the Me ligand *trans* to the iodo ligand. Two SbMe resonances are evident both in the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra for the Me-substituted distibine complexes, consistent with the distinct environments experienced by the SbMe groups, one oriented towards a Me ligand, the other towards the iodo ligand. In some cases the <sup>195</sup>Pt coupling through the quadrupolar antimony centres is evident in

the proton and/or carbon-13 NMR spectra, *e.g.* in  $[(PtMe_3)_2(\mu-Me_2SbCH_2SbMe_2)(\mu-I)_2]$  where three bond Pt–H couplings of 3–4 Hz are clearly evident on the SbMe and SbCH<sub>2</sub> resonances in the <sup>1</sup>H NMR spectrum.

The Pt(IV) species each show a single <sup>195</sup>Pt NMR resonance at ca. -4400 ppm, some 400 ppm to high frequency of the corresponding dimethyl-Pt(II) species (Table 1). The <sup>195</sup>Pt NMR shifts for related methyl Pt(II) and -(IV) phosphines and arsines show similar trends with oxidation state, although the nature of the Group 15 donor atom type has a significant effect. Thus, the  $\delta$ <sup>(195</sup>Pt) values for [PtMe<sub>3</sub>I(PMe<sub>2</sub>Ph)<sub>2</sub>] and [PtMe<sub>3</sub>I(SbMe<sub>2</sub>Ph)<sub>2</sub>] respectively are -4277 ppm and -4471 ppm, while those for  $[PtMe_3I(PMePh_2)_2]$  and  $[PtMe_3I(SbMePh_2)_2]$  are -4227 and -4582 ppm respectively,<sup>16</sup> consistent with incorporation of the heavier Sb atom in place of P. The  $\delta$ <sup>(195</sup>Pt) values for the dinuclear  $[(PtMe_3)_2(\mu-R_2SbCH_2SbR_2)(\mu-I)_2]$  (R = Ph, -4360; R = Me, -4509 ppm) are not significantly shifted from the mononuclear [PtMe<sub>3</sub>I(L–L)], despite the different donor set (Me<sub>3</sub>I<sub>2</sub>Sb in the former vs. Me<sub>3</sub>ISb<sub>2</sub> in the latter). This suggests that replacement of a heavy I ligand by another heavy atom (Sb) has a negligible electronic effect. This so-called 'heavy atom effect' has been seen before in e.g.  $[PtI_3(SbMe_3)]^-$  (I<sub>3</sub>Sb coordination;  $\delta^{195}Pt = -5642$ ) and  $[PtI_2(SbMe_3)_2]$  (I<sub>2</sub>Sb<sub>2</sub> coordination;  $\delta^{195}Pt = -5815$ ).<sup>17</sup> The  ${}^{1}J_{\text{Pt-C}}$  coupling constants in this series of Pt(IV) stibines are *ca*. 550 to 650 Hz, the larger couplings usually occurring for the Me ligand trans to iodine as expected.

Detailed studies have been undertaken by Puddephatt and co-workers and others on the chemistry of alkyl-Pt complexes with phosphine ligands. They have shown that oxidative addition of MeI to dimethyl-Pt(II) phosphine species invariably yield the corresponding [PtMe<sub>3</sub>I(diphosphine)]. These trimethyl–Pt(IV) phosphine complexes then readily undergo reductive elimination of ethane upon thermolysis.<sup>18</sup> We have also found that treating a solution of [PtMe<sub>2</sub>{Me<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbMe<sub>2</sub>}] with MeI in d<sup>6</sup>benzene leads to essentially quantitative conversion (by <sup>1</sup>H NMR spectroscopy) to [PtMe<sub>3</sub>I{Me<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbMe<sub>2</sub>}]. Also, thermogravimetric analysis of [PtMe<sub>3</sub>I(SbPh<sub>3</sub>)<sub>2</sub>] shows a mass loss at ca. 170 °C consistent with reductive elimination of ethane. Thus, despite the anticipated fragility of the Sb-C linkages, the stibine ligands do support both Pt(II) and Pt(IV) centres, readily giving the products in high yields. These can then undergo oxidative addition/reductive elimination reaction chemistry. This contrasts with previous work on the Pt(IV) tetrachloro distibine complexes, [PtCl<sub>4</sub>(distibine)], which are extremely unstable. The difference in



Pt1-C29 Pt1-C30 2.069(13) 2.098(11)2.6025(11) Pt1-C28 2.106(12) Pt1-Sb1 Pt1-Sb2 2.6342(11) Pt1-I1 2.7830(11) 2.120(12) 2.122(12) Sb1-C7 Sb1-C1 Sb1-C13 2.162(12) Sb2-C16 2.109(13) 2.136(11) Sb2-C15 2.159(11) Sb2-C22 C30-Pt1-C29 87.7(5) C30-Pt1-C28 88.0(5) C29-Pt1-C28 84.4(5) C30-Pt1-Sb1 91.8(3) C29-Pt1-Sb1 92.8(3) C28-Pt1-Sb1 177.2(3) 92.2(4) C30-Pt1-Sb2 C29-Pt1-Sb2 179.5(3) C28-Pt1-Sb2 95.1(3) Sb1-Pt1-Sb2 87.68(3) 179.2(3) C30-Pt1-I1 C29-Pt1-I1 92.8(4) C28-Pt1-I1 91.5(4) Sb1-Pt1-I1 88.79(3) Sb2-Pt1-I1 87.29(4) C1-Sb1-C7 98.4(4)C1-Sb1-C13 99.8(5) C7-Sb1-C13 102.4(5)C1-Sb1-Pt1 120.8(3) C7-Sb1-Pt1 114.7(3)C13-Sb1-Pt1 117.4(3) C16-Sb2-C22 98.3(4) C16-Sb2-C15 101.8(5) C22-Sb2-C15 100.5(4)C16-Sb2-Pt1 117.4(3)C22-Sb2-Pt1 118.5(3) C15-Sb2-Pt1 117.0(3)

Table 2 Selected bond lengths (Å) and angles (°) for  $[PtMe_3\{Ph_2Sb-(CH_2)_3SbPh_2\}I]$ 

stability is therefore attributed to significantly stronger ligand field effects in the Pt-methyl complexes reported here.

#### Crystal structures

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Crystal structure determinations have been undertaken on five representative examples of the Pt(IV) stibine complexes to provide unambiguous assignment of their geometries and to allow comparisons between these, the first structurally characterised examples of stibine complexes involving a formally Pt(IV) centre, and literature examples incorporating Pt(II) centres. The structure of [PtMe<sub>3</sub>{Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}] shows (Fig. 1, Table 2) a distorted octahedral Pt(IV) centre coordinated to three *fac* Me groups, one I ligand and two Sb atoms from a chelating distibine. [PtMe<sub>3</sub>{Me<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbMe<sub>2</sub>}I] adopts a very similar arrangement (Fig. 2, Table 3), although in this species the Pt centre, C4, C5 and I1 occupy a crystallographic mirror plane which bisects the distibine ligand. Very similar geometries are observed for [PtMe<sub>3</sub>{ $o-C_6H_4(CH_2SbMe_2)_2$ }I] (Fig. 3, Table 4) and [PtMe<sub>3</sub>(SbPh<sub>3</sub>)<sub>2</sub>I] (Fig. 4, Table 5).



Fig. 1 View of the structure of  $[PtMe_3{Ph_2Sb(CH_2)_3SbPh_2}I]$  with numbering scheme adopted. H atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level.

The Sb-Pt(IV) bond distances in all of the chelated distibine complexes lie in the range 2.6025(11)-2.6342(11) Å, signi-

Table 3 Selected bond lengths (Å) and angles (°) for  $[PtMe_3\{Me_2Sb-(CH_2)_3SbMe_2\}I]^{\alpha}$ 

Pt1–C5 Pt1–Sb1 Sb1–C1 Sb1–C3	2.081(9) 2.6217(7) 2.117(7) 2.133(6)	Pt1–C6 Pt1–I1 Sb1–C2	2.145(6) 2.7850(11) 2.130(6)
$\begin{array}{c} C5-Pt1-C6\\ C5-Pt1-Sb1\\ C6a-Pt1-Sb1\\ C5-Pt1-I1\\ Sb1-Pt1-I1\\ C1-Sb1-C3\\ C1-Sb1-Pt1\\ C3-Sb1-Pt1\\ C3-Sb1-Pt1\\ \end{array}$	86.9(3) 93.91(19) 93.08(19) 176.6(3) 88.524(16) 100.4(3) 116.3(2) 117.08(19)	C6-Pt1-C6a C6-Pt1-Sb1 Sb1-Pt1-Sb1a C6-Pt1-I1 C1-Sb1-C2 C2-Sb1-C3 C2-Sb1-Pt1	84.2(4) 177.11(18) 89.63(3) 90.54(18) 100.0(3) 98.3(3) 121.0(2)

<sup>*a*</sup> Symmetry operation:  $a = x, \frac{1}{2} - y, z$ .



**Fig. 2** View of the structure of  $[PtMe_3\{Me_2Sb(CH_2)_3SbMe_2\}I]$  with numbering scheme adopted. H atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level. There is a mirror plane passing through Pt1, I1, C4 and C5. Symmetry operation:  $a = x, \frac{1}{2} - y, z$ .



Fig. 3 View of the structure of  $[PtMe_3{o-C_6H_4(CH_2SbMe_2)_2}]$  with numbering scheme adopted. H atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level.

ficantly longer than in the Pt(II) distibines,<sup>19</sup> *e.g.* [PtCl<sub>2</sub>{ $o-C_6H_4(CH_2SbMe_2)_2$ ] (2.4860(7), 2.4931(8) Å) and [Pt{ $o-C_6H_4(CH_2SbMe_2)_2$ ]<sup>2+</sup> (2.5690(8)–2.5802(8) Å)—although of course the higher coordination number in the Pt(IV) species and the strong *trans* influence of the Me groups will both have a

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Table 4 Selected bond lengths (Å) and angles (°) for  $[PtMe_3\{o-C_6H_4(CH_2SbMe_2)_2\}I]$ 

Pt1–C14	2.078(5)	Pt1–C13	2.108(5)
Pt1-C15	2.113(5)	Pt1–Sb2	2.6052(4)
Pt1–Sb1	2.6204(5)	Pt1–I1	2.7808(5)
Sb1-C1	2.119(5)	Sb1-C2	2.146(5)
Sb1–C3	2.154(4)	Sb2-C12	2.126(5)
Sb2-C11	2.138(5)	Sb2-C10	2.144(4)
C14-Pt1-C13	84.8(2)	C14-Pt1-C15	86.9(2)
C13-Pt1-C15	89.2(2)	C14-Pt1-Sb2	94.71(16)
C13-Pt1-Sb2	88.42(14)	C15-Pt1-Sb2	176.95(15)
C14-Pt1-Sb1	96.50(15)	C13-Pt1-Sb1	175.98(14)
C15-Pt1-Sb1	87.11(15)	Sb2-Pt1-Sb1	95.246(11)
C14-Pt1-I1	178.33(16)	C13-Pt1-I1	94.21(15)
C15-Pt1-I1	94.41(15)	Sb2-Pt1-I1	83.901(15)
Sb1–Pt1–I1	84.562(11)	C1-Sb1-C2	100.4(2)
C1-Sb1-C3	98.93(19)	C2-Sb1-C3	100.50(19)
C1-Sb1-Pt1	113.82(15)	C2-Sb1-Pt1	120.18(14)
C3-Sb1-Pt1	119.35(12)	C12-Sb2-C11	101.9(2)
C12-Sb2-C10	100.71(18)	C11-Sb2-C10	100.7(2)
C12-Sb2-Pt1	113.54(14)	C11-Sb2-Pt1	119.84(15)
C10-Sb2-Pt1	117.24(13)		



**Fig. 4** View of the structure of one of the crystallographically independent molecules of  $[PtMe_3(SbPh_3)_2I]$  with numbering scheme adopted (the other molecule in the asymmetric unit is essentially indistinguishable). H atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level. There is disorder in the I2–Pt2–C77 unit (see text). The figure shows the major component.

significant effect on d(Pt-Sb). The Sb–Pt–Sb angles in the Pt(IV) stibine complexes reflect the different chelate ring sizes, with the  $o-C_6H_4(CH_2SbMe_2)_2$  ligand (seven-membered ring chelate) giving a wide angle of 95.246(11)°, whereas the Sb–Pt–Sb angles within the six-membered chelates are <90°. The same trend is seen in the non-bonded Sb…Sb distances within the chelates. Thus,  $d(Sb \cdots Sb)$  is *ca.* 0.17 Å greater for the  $o-C_6H_4(CH_2SbMe_2)_2$  complex *vs.* the R<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbR<sub>2</sub> complexes. The Pt–Sb distances (2.6457(7)–2.6656(7) Å), Sb–Pt–Sb angles (96.48(2), 96.74(2)°) in [PtMe<sub>3</sub>I(SbPh<sub>3</sub>)<sub>2</sub>] are similar to those in the wide-angle xylyl–distibine complex, consistent with the substantial steric requirements of the bulky SbPh<sub>3</sub> groups in the former.

The Pt-C<sub>transSb</sub> distances are all *ca.* 2.1 Å, and longer than  $d(Pt-C)_{trans1}$ , consistent with the stibine exerting a stronger *trans* influence than iodide. We have observed previously that the C–Sb–C angles within the stibine ligands SbPh<sub>3</sub> and Ph<sub>2</sub>SbCH<sub>2</sub>SbPh<sub>2</sub>

Pt2-C78 2.098(9) Pt2-C76 2.102(9)Pt2-C77 2.5679(14)<sup>b</sup> Pt2-I2 2.6302(12)b Pt2-Sb4 2.6551(7) Pt2-Sb3 2.6651(7)Sb3-C40 2.137(8)Sb3-C52 2.143(8)Sb3-C46 2.143(9)Sb4-C70 2.131(8) Sb4-C58 2.132(9) Sb4-C64 2.149(8) C78-Pt2-C77 C78-Pt2-C76 85.3(4)  $87.4(4)^{b}$ C76-Pt2-C77  $87.0(4)^{b}$ C78-Pt2-I2  $86.8(4)^{b}$ C76-Pt2-I2  $85.5(4)^{b}$ C77-Pt2-I2  $170.81(4)^{b}$ C78-Pt2-Sb4 171.4(3) C76-Pt2-Sb4 86.7(3) C77-Pt2-Sb4 95.31(3)<sup>b</sup> I2-Pt2-Sb4 89.46(3)b C78-Pt2-Sb3 91.7(3) C76-Pt2-Sb3 174.3(3) C77-Pt2-Sb3 88.07(3) I2-Pt2-Sb3 99.21(3)<sup>b</sup> Sb4-Pt2-Sb3 96.48(2) C40-Sb3-C52 98.1(3) C40-Sb3-C46 98.1(3) C52-Sb3-C46 99.6(3) C40-Sb3-Pt2 115.3(2)C52-Sb3-Pt2 117.1(2)C46-Sb3-Pt2 124.0(2) C70-Sb4-C58 C70-Sb4-C64 100.2(3)98.8(3) C58-Sb4-C64 101.3(3) C70-Sb4-Pt2 111.4(2)C58-Sb4-Pt2 120.7(2)C64-Sb4-Pt2 120.6(2)

Table 5 Selected bond lengths (Å) and angles (°) for [PtMe<sub>3</sub>(SbPh<sub>3</sub>)<sub>2</sub>I]<sup>a</sup>

<sup>*a*</sup> Bond lengths and angles for the second molecule involving Pt1, I1, Sb1, Sb2 and C1–C39 are similar and also have disorder in the *trans* I1–Pt1–C fragment. <sup>*b*</sup> Disordered group I2/C77A–Pt2–C77/I2A with chemically unreliable bond lengths and angles (see text). This is most marked in the Pt2–C77 bond length when compared with other Pt–C distances.

open by up to *ca.* 8° upon coordination to a medium oxidation state transition metal centre, a consequence of the rehybridisation which takes place at antimony upon coordination to a metal centre.<sup>20</sup> Comparison of the data reported *vs.* the C–Sb–C angles in known Pt(II) stibines show that the angles are essentially unaffected by the change in oxidation state.

The structure of  $[(PtMe_3I)_2(Ph_2SbCH_2SbPh_2)]$  confirms (Fig. 5, Table 6) that the distibine ligand bridges two PtMe<sub>3</sub> fragments, with two bridging iodo ligands completing the distorted octahedral coordination environment at each Pt centre, giving an edge shared bioctahedral structure. This is consistent with the solution structure deduced from the NMR spectroscopic data. The Pt–Sb bond distances of 2.6530(5) and 2.6793(5) Å are longer (by *ca.* 0.05 Å) than those in the mononuclear species above. This may

Fig. 5 View of the structure of  $[(PtMe_3I)_2(Ph_2SbCH_2SbPh_2)]$  with numbering scheme adopted. H atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level.

	e ()		- /- ( -	/-			
Pt1-C2 Pt1-C3 Pt1-I2 Pt2-C30	2.057(5) 2.066(6) 2.7929(4) 2.070(6)	Pt1-C1 Pt1-Sb1 Pt1-I1 Pt2-C31	2.065(6) 2.6530(5) 2.7979(5) 2.070(6)	Pt2–I1 Sb1–C4 Sb1–C16 Sb2–C16	2.7957(4) 2.132(5) 2.139(5) 2.140(5)	Pt2–I2 Sb1–C10 Sb2–C17 Sb2–C23	2.8034(5) 2.136(5) 2.120(5) 2.142(5)
Pt2–C29	2.076(6)	Pt2–Sb2	2.6793(5)				
C2-Pt1-C1 C1-Pt1-C3 C1-Pt1-Sb1 C2-Pt1-12 C3-Pt1-12 C2-Pt1-11 C3-Pt1-11 I2-Pt1-11 I2-Pt1-11 C30-Pt2-C29	87.7(2) 85.0(2) 178.38(17) 174.89(18) 94.67(17) 90.99(17) 177.92(18) 85.713(12) 85.1(3)	C2-Pt1-C3 C2-Pt1-Sb1 C3-Pt1-Sb1 C1-Pt1-I2 Sb1-Pt1-I2 C1-Pt1-I1 Sb1-Pt1-I1 C30-Pt2-C31 C31-Pt2-C29	88.5(2) 93.22(17) 93.66(18) 88.56(17) 90.593(12) 92.92(17) 88.383(12) 88.0(2) 86.5(3)	C31-Pt2-I1 Sb2-Pt2-I1 C31-Pt2-I2 Sb2-Pt2-I2 Pt2-I1-Pt1 C4-Sb1-C10 C10-Sb1-C16 C10-Sb1-Pt1 C17-Sb2-C16	89.94(18) 90.224(12) 91.36(18) 85.759(12) 94.184(12) 101.04(19) 100.3(2) 118.30(14) 100.4(2)	C29-Pt2-I1 C30-Pt2-I2 C29-Pt2-I2 I1-Pt2-I2 Pt1-I2-Pt2 C4-Sb1-C16 C4-Sb1-Pt1 C16-Sb1-Pt1 C17-Sb2-C23	176.42(18) 179.34(17) 95.00(18) 85.556(12) 94.123(12) 99.01(19) 117.90(14) 116.88(14) 100.29(19)
C30-Pt2-Sb2 C29-Pt2-Sb2	94.88(17) 93.34(18)	C31-Pt2-Sb2 C30-Pt2-I1	177.09(18) 94.26(17)	C16-Sb2-C23 C16-Sb2-Pt2	93.96(18) 115.89(14)	C17-Sb2-Pt2 C23-Sb2-Pt2	120.13(14) 121.29(14)

 Table 6
 Selected bond lengths (Å) and angles (°) for [(PtMe<sub>3</sub>I)<sub>2</sub>(Ph<sub>2</sub>SbCH<sub>2</sub>SbPh<sub>2</sub>)]

be a consequence of the short  $C_1$ -linked distibute ligand having difficulty in spanning the two Pt centres. The rather open Sb1–C16–Sb2 angle (116.2(2)°) is also consistent with this.

## Conclusions

These results show that stibine ligands can bond effectively to organometallic fragments in both high and medium oxidation states, affording the first series of alkyl Pt(II) and Pt(IV) stibines which readily undergo oxidative addition of MeI or reductive elimination of ethane respectively. The high yield formation of this series of stable trimethyl Pt(IV) stibine complexes contrasts with the very unstable tetrachloro Pt(IV) species [PtCl<sub>4</sub>(distibine)]. Further work to examine in more detail the reaction chemistry of distibine ligands with organometallic reagents is underway—an area of work very much in its infancy.

## Experimental

Mass spectra were run by positive ion electrospray (MeCN solution) using a VG Biotech platform. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> (unless otherwise stated) using a Bruker AV300 spectrometer. <sup>13</sup>C{<sup>1</sup>H} and <sup>195</sup>Pt{<sup>1</sup>H} NMR spectra (ppm) were recorded in CDCl<sub>3</sub> (unless otherwise stated), using a Bruker DPX400 spectrometer operating at 100.6 or 85.62 MHz respectively and are referenced to TMS and external 1 mol dm<sup>-3</sup> Na<sub>2</sub>[PtCl<sub>6</sub>] respectively. Microanalyses were undertaken by the University of Strathclyde microanalytical service.

Solvents were dried prior to use and all preparations were undertaken using standard Schlenk techniques under a N<sub>2</sub> atmosphere. [PtMe<sub>3</sub>I]<sub>4</sub>,<sup>21</sup> [PtMe<sub>2</sub>(cod)],<sup>22</sup> [PtMe<sub>2</sub>(SMe<sub>2</sub>)<sub>2</sub>]<sup>23</sup> and the stibine ligands were prepared as described previously.<sup>24-26</sup>

#### Platinum(II) compounds

### $[PtMe_2{Ph_2Sb(CH_2)_3SbPh_2}]$

Method a. [Me<sub>2</sub>Pt(cod)] (0.042 g, 0.125 mmol) and Ph<sub>2</sub>Sb-(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub> (0.075 g, 0.125 mmol) were dissolved in toluene (15 cm<sup>3</sup>) and stirred under N<sub>2</sub> for 12 h. The resulting yellow solution was filtered, reduced in volume to  $\sim$ 1 cm<sup>3</sup> and hexane (10 cm<sup>3</sup>) was added to precipitate a solid. The solution was decanted off and the yellow solid dried *in vacuo* (yield: 70%).

Required for  $[C_{29}H_{32}PtSb_2]$ : C, 42.5; H, 3.9. Found: C, 42.6; H, 3.8%. <sup>1</sup>H NMR: 1.05 (s, 6H, Me  ${}^2J_{PtH} = 85$  Hz), 2.40–2.15 (m, 6H, CH<sub>2</sub>), 7.1–7.6 (m, 20H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR: -3.63 (2C, Me,  ${}^1J_{PtC} =$  716 Hz), 18.57 (2C, CH<sub>2</sub>Sb), 23.99 (1C, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 129.21, 130.04, 131.41, 135.91 (Ph).

*Method b.*  $[Me_2Pt(SMe_2)_2]$  (0.060 g, 0.17 mmol) and  $Ph_2Sb(CH_2)_3SbPh_2$  (0.1 g, 0.17 mmol) were dissolved in dry CHCl<sub>3</sub> (15 cm<sup>3</sup>) and stirred at RT for 1 h. The excess solvent was removed under reduced pressure, and the residues were triturated with hexane to afford a pale yellow solid. This was then dried *in vacuo.* <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy as for method a.

[PtMe<sub>2</sub>{Me<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbMe<sub>2</sub>}]. [Me<sub>2</sub>Pt(SMe<sub>2</sub>)<sub>2</sub>] (0.060 g, 0.17 mmol) and Me<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbMe<sub>2</sub> (0.058 g, 0.17 mmol) were dissolved in dry C<sub>6</sub>H<sub>6</sub> (5 cm<sup>3</sup>) and stirred at RT for 15 minutes. The excess solvent was removed under reduced pressure, and the residues were triturated with hexane to afford a pale yellow oil which was dried *in vacuo* (yield: 65%). ES<sup>+</sup> MS (MeCN): 555 ([<sup>195</sup>PtMe{Me<sub>2</sub><sup>121</sup>Sb(CH<sub>2</sub>)<sub>3</sub><sup>123</sup>SbMe<sub>2</sub>]]<sup>+</sup> 556). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 0.70 (s, 12H, SbMe, <sup>3</sup>J<sub>PtH</sub> = 7 Hz), 1.14 (m, 6H, CH<sub>2</sub>), 1.48 (s, 6H, Me, <sup>2</sup>J<sub>PtH</sub> = 83 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): -6.1 (4C, SbMe), -4.98 (2C, Me), 15.26 (2C, CH<sub>2</sub>Sb), 24.47 (1C, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).

[PtMe<sub>2</sub>{ $o-C_6H_4(CH_2SbMe_2)_2$ ]]. Method as for [PtMe<sub>2</sub>-{ $Me_2Sb(CH_2)_3SbMe_2$ ]]. Pale yellow solid (yield: 63%). Required for [C<sub>14</sub>H<sub>26</sub>PtSb<sub>2</sub>]·0.5C<sub>6</sub>H<sub>14</sub>: C, 30.2; H, 4.9. Found: C, 30.3; H, 4.1%. ES<sup>+</sup> MS (MeCN): 658 ([<sup>195</sup>Pt{ $o-C_6H_4(CH_2^{121/123}SbMe_2)_2$ }-(MeCN)]<sup>+</sup> 659), 617 ([<sup>195</sup>PtMe{ $o-C_6H_4(CH_2^{121/123}SbMe_2)_2$ }]<sup>+</sup> 618). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 0.73 (s, 12H, SbMe, <sup>3</sup>J<sub>PtH</sub> = 9 Hz), 1.26 (s, 6H, Me, <sup>2</sup>J<sub>PtH</sub> = 82 Hz), 2.88 (br, 4H, CH<sub>2</sub>), 6.6–6.9 (m, 4H, Ar–H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): -5.55 (4C, SbMe), -3.85 (2C, Me, <sup>1</sup>J<sub>PtC</sub> = 726 Hz), 23.15 (2C, CH<sub>2</sub>).

**[(PtMe<sub>2</sub>)<sub>2</sub>(Ph<sub>2</sub>SbCH<sub>2</sub>SbPh<sub>2</sub>)<sub>2</sub>].** Method as for [PtMe<sub>2</sub>{Me<sub>2</sub>-Sb(CH<sub>2</sub>)<sub>3</sub>SbMe<sub>2</sub>}]. Pale yellow solid (yield: 70%). Required for [C<sub>54</sub>H<sub>56</sub>Pt<sub>2</sub>Sb<sub>4</sub>]-0.5C<sub>6</sub>H<sub>6</sub>: C, 42.2; H, 3.7. Found: C, 42.4; H, 3.6%. ES<sup>+</sup> MS (MeCN): 1569 ([<sup>195</sup>Pt<sub>2</sub>Me<sub>3</sub>(Ph<sub>2</sub>)<sup>121</sup>SbCH<sub>2</sub>)<sup>123</sup>SbPh<sub>2</sub>)<sub>2</sub>]<sup>+</sup> 1567), 1341 ([<sup>195</sup>PtMe(Ph<sub>2</sub>)<sup>121</sup>SbCH<sub>2</sub>)<sup>123</sup>SbPh<sub>2</sub>)<sub>2</sub>]<sup>+</sup> 1342). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 1.43 (s, 6H, Me, <sup>2</sup>J<sub>PtH</sub> = 82 Hz), 2.20 (br, 2H, CH<sub>2</sub>), 6.9–7.4 (m, 20H, Ph).

 $[(PtMe_2)_2(Me_2SbCH_2SbMe_2)_2]$ . Method as for  $[PtMe_2\{Me_2-Sb(CH_2)_3SbMe_2\}]$ . Pale yellow solid (yield: 55%). ES<sup>+</sup> MS (MeCN): 1071 ([<sup>195</sup>Pt\_2Me\_3(Me\_2<sup>121</sup>SbCH\_2<sup>123</sup>SbMe\_2)\_2]<sup>+</sup> 1071), 845

 $([^{195}PtMe(Me_2^{121}SbCH_2^{123}SbMe_2)_2]^+$  846). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 0.95 (s, 12H, SbMe,  ${}^{3}J_{PtH} = 6$  Hz), 1.17 (s, 6H, Me,  ${}^{2}J_{PtH} = 80$  Hz), 1.27 (s, 2H, CH<sub>2</sub>).  ${}^{13}C{}^{1}H{}$  NMR (C<sub>6</sub>D<sub>6</sub>): -5.89 (4C, SbMe), -3.96  $(2C, Me, {}^{1}J_{PtC} = 711 \text{ Hz}), -3.46 (1C, CH_2).$ 

### Platinum(IV) compounds

 $[PtMe_3{Ph_2Sb(CH_2)_3SbPh_2}]I]$ . Me<sub>3</sub>PtI (0.065 g, 0.177 mmol) and Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub> (0.105 g, 0.177 mmol) were dissolved in dry CHCl<sub>3</sub> (20 cm<sup>3</sup>) under argon and refluxed for 4 h. The light yellow solution was then pumped to dryness in vacuo to give a light yellow waxy solid which was triturated with hexane to produce a light yellow powder (yield: 80 mg, 50%). Required for [C<sub>30</sub>H<sub>35</sub>IPtSb<sub>2</sub>]·0.5CHCl<sub>3</sub>: C, 35.9; H, 3.5. Found: C, 36.4; H, 4.0%. <sup>1</sup>H NMR: 1.20 (s, 3H, Me trans I, 72 Hz), 1.70 (s, 6H, Me trans Sb, 65 Hz), 2.10-2.80 (m, 6H, CH<sub>2</sub>), 7.20-7.75 (m, 20H, Ph).  ${}^{13}C{}^{1}H}$  NMR: -3.17 (C, Me trans I, 616 Hz), 5.31 (2C, Me trans Sb, 575 Hz), 18.30 (2C, SbCH<sub>2</sub>), 24.12 (1C, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 127.23-136.90 (Ph).

 $[PtMe_3{Me_2Sb(CH_2)_3SbMe_2}]I]$ . Method as above. Yellow solid (yield: 45%). Required for [C<sub>10</sub>H<sub>27</sub>IPtSb<sub>2</sub>]: C, 16.8; H, 3.8. Found: C, 16.3; H, 3.9%. ES+ MS (MeCN): 596 ([195PtMe-{ $Me_2^{121}Sb(CH_2)_3^{123}SbMe_2$ }(MeCN)]<sup>+</sup> 597), 555 ([<sup>195</sup>PtMe{ $Me_2^{121}$ -Sb(CH<sub>2</sub>)<sub>3</sub><sup>123</sup>SbMe<sub>2</sub>}]<sup>+</sup> 556). <sup>1</sup>H NMR: 0.97 (s, 6H, SbMe), 1.07 (s, 3H, Me trans I, 78 Hz), 1.27 (s, 6H, SbMe), 1.45 (s, 6H, Me trans Sb, 65 Hz), 2.0 (m, 6H, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR: -11.22 (2C, SbMe), -7.58 (2C, SbMe), -6.20 (C, Me trans I, 628 Hz), 1.85 (2C, Me trans Sb, 553 Hz), 14.31 (2C, SbCH<sub>2</sub>), 24.30 (1C, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).

 $[PtMe_3{o-C_6H_4(CH_2SbMe_2)_2}]$ I]. Method as above. Yellow solid (yield: 60%). Required for  $[C_{15}H_{29}IPtSb_2]$ .  $\frac{1}{4}C_6H_{14}$ : C, 24.9; H, 4.1. Found: C, 24.7; H, 3.7%. <sup>1</sup>H NMR: 0.78 (s, 6H, SbMe), 0.82 (s, 3H, Me trans I, 76 Hz), 1.20 (s, 6H, Me trans Sb, 65 Hz), 1.31 (s, 6H, SbMe), 3.12 (m, 2H, CH<sub>2</sub>), 4.08 (d, 2H, CH<sub>2</sub>), 6.88-7.05 (m, 4H, o-C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR: -11.57 (2C, SbMe), -6.20 (C, Me trans I, 611 Hz), -6.05 (2C, SbMe), 3.82 (2C, Me trans Sb, 562 Hz), 21.37 (2C, SbCH<sub>2</sub>), 126.16, 130.53, 136.45 (o-C<sub>6</sub>H<sub>4</sub>).

[(PtMe<sub>3</sub>I)<sub>2</sub>(Ph<sub>2</sub>SbCH<sub>2</sub>SbPh<sub>2</sub>)]. Method as above, using a Pt : Ph<sub>2</sub>SbCH<sub>2</sub>SbPh<sub>2</sub> ratio of 2 : 1. Yellow solid (yield: 50%). Required for [C<sub>31</sub>H<sub>40</sub>I<sub>2</sub>Pt<sub>2</sub>Sb<sub>2</sub>]: C, 28.6; H, 3.1. Found: C, 29.4; H, 3.1%. <sup>1</sup>H NMR: 1.36 (s, 12H, Me trans I, 76 Hz), 2.25 (s, 6H, Me trans Sb, 69 Hz), 2.92 (2H, CH<sub>2</sub>), 7.10–7.40 (m, 20H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR: 5.53 (2C, Me trans I, 655 Hz), 8.27 (C, Me trans Sb, 694 Hz), 14.70 (1C, SbCH<sub>2</sub>), 138.8-128.8 (Ph).

[(PtMe<sub>3</sub>I)<sub>2</sub>(Me<sub>2</sub>SbCH<sub>2</sub>SbMe<sub>2</sub>)]. Method as above, using a Pt : Me<sub>2</sub>SbCH<sub>2</sub>SbMe<sub>2</sub> ratio of 2:1. Yellow solid (yield: 55%). Required for [C<sub>11</sub>H<sub>32</sub>I<sub>2</sub>Pt<sub>2</sub>Sb<sub>2</sub>].1/3 C<sub>6</sub>H<sub>14</sub>: C, 14.4; H, 3.4. Found: C, 14.6; H, 3.6%. <sup>1</sup>H NMR: 1.18 (s, 12H, SbMe, 3 Hz), 1.23 (s, 12H, Me trans I, 76 Hz), 2.04 (s, 6H, Me trans Sb, 67 Hz), 2.28 (2H, CH<sub>2</sub>, 4.5 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR: -6.91 (4C, SbMe), -0.05 (C, SbCH<sub>2</sub>), 4.17 (2C, Me trans I, 925 Hz), 12.78 (1C, Me trans Sb, 571 Hz).

Method as above, giving a light yellow oil (yield: 70%). <sup>1</sup>H NMR: 0.93 (s, 3H, Me trans I, 71 Hz), 1.21 (s, 6H, SbMe), 1.43 (s, 6H, Me trans Sb, 66 Hz), 7.30–7.40 (m, 10H, Ph).  ${}^{13}C{}^{1}H$  NMR: -5.87 (1C, Me trans I, 643 Hz), -2.98 (2C, SbMe), 5.16 (2C, Me trans Sb, 564 Hz), 129.23, 129.92, 134.73 (Ph).

[PtMe<sub>3</sub>(SbMePh<sub>2</sub>)<sub>2</sub>I]. Method as above. Yellow solid (yield: 55%). Required for [C<sub>29</sub>H<sub>35</sub>IPtSb<sub>2</sub>]: C, 36.7; H, 3.7. Found: C,

	[PtMe <sub>3</sub> {Ph <sub>2</sub> Sb(CH <sub>2</sub> ) <sub>3</sub> SbPh <sub>2</sub> }I]	$[PtMe_3\{Me_2Sb(CH_2)_3SbMe_2\}I]$	$[PtMe_3\{o-C_6H_4(CH_2SbMe_2)_2\}I]$	[PtMe <sub>3</sub> (SbPh <sub>3</sub> ) <sub>2</sub> I]	[(Me <sub>3</sub> PtI) <sub>2</sub> (Ph <sub>2</sub> SbCH <sub>2</sub> SbPh <sub>2</sub> )]
Formula	$C_{30}H_{35}IPtSb_2$	$\mathrm{C_{10}H_{27}IPtSb_2}$	$ m C_{15}H_{29} m IPtSb_2$	$C_{39}H_{39}IPtSb_2$	${ m C}_{31}{ m H}_{40}{ m I}_2{ m Pt}_2{ m Sb}_2$
M	961.07	712.81	774.87	1073.19	1300.11
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	<i>Pnna</i> (no. 62)	$P2_1/c$ (no. 14)	<i>P</i> 1 (no. 2)	<i>P</i> 1 (no. 2)
aíÅ	12.611(3)	14.035(4)	11.7559(16)	9.6674(10)	9.7960(10)
$b/\text{\AA}$	12.557(5)	10.851(3)	9.2374(12)	18.681(3)	11.7470(10)
c/Å	19.535(5)	11.349(2)	19.124(2)	19.993(3)	15.3850(10)
$a/^{\circ}$	00	90	90	81.604(7)	103.790(6)
β/°	105.48(2)	90	102.258(6)	89.966(8)	93.514(5)
y / 0	<u> </u>	90	90	83.681(8)	90.628(4)
$U/Å^3$	2981.4(16)	1728.4(8)	2029.4(5)	3549.7(7)	1715.5(3)
Z	4	4	4	4	2
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	7.532	12.937	11.030	6.338	11.504
Rint	0.1915	0.0611	0.0336	0.0943	0.0299
Total no. refins.	41792	10988	18921	75972	33362
Unique reflections	6924	2081	4624	16313	7793
No. of parameters	307	74	172	777	334
$R1 [I_0 > 2\sigma(I_0)]$	0.0600	0.0346	0.0252	0.0572	0.0284
R1 [all data]	0.1687	0.0558	0.0314	0.1066	0.0320
$wR_2 \left[ I_{\rm o} > 2\sigma(I_{\rm o}) \right]$	0.0968	0.0644	0.0573	0.0906	0.0851
$wR_2$ [all data]	0.1236	0.0703	0.0598	0.1031	0.0879

36.2; H, 3.7%. <sup>1</sup>H NMR: 1.08 (s, 3H, Me *trans* I, 71 Hz), 1.38 (s, 3H, SbMe), 1.55 (s, 6H, Me *trans* Sb, 67 Hz), 7.10–7.40 (m, 20H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR: -5.05 (1C, Me *trans* I, 611 Hz), -1.73 (1C, SbMe), 7.60 (2C, Me *trans* Sb, 566 Hz), 129.0–136.9 (Ph).

[PtMe<sub>3</sub>(SbPh<sub>3</sub>)<sub>2</sub>I]. Method as above. Yellow solid (yield: 70%). Required for  $[C_{39}H_{39}IPtSb_2]$ : C, 43.6; H, 3.7. Found: C, 43.4; H, 3.4%. <sup>1</sup>H NMR: 1.27 (s, 3H, Me *trans* I, 70 Hz), 1.83 (s, 6H, Me *trans* Sb, 68 Hz), 7.05–7.50 (m, 30H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR: -3.72 (1C, Me *trans* I, 606 Hz), 10.43 (2C, Me *trans* Sb, 542 Hz), 129.3–136.9 (Ph).

## X-Ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 7. Pale yellow crystals of  $[PtMe_3{Ph_2Sb(CH_2)_3SbPh_2}I], [PtMe_3{Me_2Sb(CH_2)_3SbMe_2}I],$  $[PtMe_3{oC_6H_4(CH_2SbMe_2)_2}I], [PtMe_3(SbPh_3)_2I] and [(PtMe_3I)_2-$ (Ph<sub>2</sub>SbCH<sub>2</sub>SbPh<sub>2</sub>)] were obtained by liquid diffusion of hexane into a  $CH_2Cl_2$  solution of the compound. Data collection used a Nonius Kappa CCD diffractometer (T = 120 K) and with graphite-monochromated Mo-K<sub>a</sub> X-radiation ( $\lambda = 0.71073$  Å). Structure solution and refinement were largely routine,<sup>27,28</sup> except for [PtMe<sub>3</sub>(SbPh<sub>3</sub>)<sub>2</sub>I] both molecules of which revealed some disorder of the trans-I-Pt-Me unit. This was modelled using partial atom positions, with the sum of the occupancies of the two I and two C components each being one. Distinct partial C atoms and partial I atoms could not be identified, hence these units were refined with identical atomic coordinates and atomic displacement parameters. Consequently the Pt-I and Pt-C distances in the trans-I-Pt-C units are weighted averages, and should not be used in comparative studies. The H atoms associated with the disordered Me groups were not included in the final structure factor calculation.

CCDC reference numbers 285688–285692.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b514019f

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