# Synthesis and properties of Rh(I) and Ir(I) distibine complexes with organometallic co-ligands

Michael D. Brown, William Levason, Gillian Reid\* and Michael Webster

Received 11th April 2006, Accepted 26th May 2006 First published as an Advance Article on the web 9th June 2006 DOI: 10.1039/b605198g

The first series of Rh(I) distibine complexes with organometallic co-ligands is described, including the five-coordinate [Rh(cod)(distibine)Cl], the 16-electron planar cations [Rh(cod)(distibine)]BF<sub>4</sub> and  $[Rh{Ph_2Sb(CH_2)_3SbPh_2}_2]BF_4$  and the five-coordinate  $[Rh(CO)(distibine)_2][Rh(CO)_2Cl_2]$  (distibute =  $R_2Sb(CH_2)_3SbR_2$ , R = Ph or Me, and  $o - C_6H_4(CH_2SbMe_2)_2$ ). The corresponding Ir(1) species [Ir(cod)- $(distibine)]BF_4 \ and \ [Ir\{Ph_2Sb(CH_2)_3SbPh_2\}_2]BF_4 \ have also \ been \ prepared. \ The \ complexes \ have \ been \ and \ a$ characterised by <sup>1</sup>H and <sup>13</sup>C $\{$ <sup>1</sup>H $\}$  NMR and IR spectroscopy, electrospray mass spectrometry and microanalysis. The crystal structure of the anion exchanged [Rh(CO){Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}<sub>2</sub>]PF<sub>6</sub>·3/4CH<sub>2</sub>Cl<sub>2</sub> is also described. The methyl-substituted distibine complexes are less stable than the complexes of Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>, with C–Sb fission occurring in some of the complexes of the former. The salts  $[Rh(CO){Ph_2Sb(CH_2)_3SbPh_2}_2]PF_6 and [Rh{Ph_2Sb(CH_2)_3SbPh_2}_2]BF_4 undergo oxidative addition addition addition and a statement of the statement of th$ with Br<sub>2</sub> to give the known  $[RhBr_{2}{Ph_{2}Sb(CH_{2})_{3}SbPh_{2}_{2}]^{+}}$ , while using HCl gives the same hydride complex from both precursors, which is tentatively assigned as [RhHCl<sub>2</sub>{Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}]. An unexpected further Rh(III) product from this reaction, *trans*-[RhCl<sub>2</sub>{Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}-{PhClSb(CH<sub>2</sub>)<sub>3</sub>SbClPh}]Cl, was identified by a crystal structure analysis and represents the first structurally characterised example of a chlorostibine coordinated to a metal. [Rh{Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}]BF<sub>4</sub> reacts with CO to give [Rh(CO){Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}]BF<sub>4</sub> initially, and upon further exposure this species undergoes further reversible carbonylation to give a cis-dicarbonyl species thought to be  $[Rh(CO)_{2}{Ph_{2}Sb(CH_{2})_{3}SbPh_{2}}{\kappa^{1}Sb-Ph_{2}Sb(CH_{2})_{3}SbPh_{2}}]BF_{4}$  which converts back to the monocarbonyl complex when the CO atmosphere is replaced with N<sub>2</sub>.

# Introduction

With the exception of the commercially available triphenylstibine, SbPh<sub>3</sub>, the coordination chemistry and organometallic chemistry of organoantimony ligands has been relatively little studied in comparison to the lighter Group 15 analogues, especially phosphines.<sup>1,2</sup> Traditionally stibines were regarded as 'poorer' ligands compared to phosphines and arsines. However, more recently, work from a number of groups has shown that the distinctly different electronic properties of the stibines can promote markedly different reaction chemistry and, in fact they are superior ligands for certain reactions. For example, the pioneering work of Werner which led to the first discovery of bridging ER<sub>3</sub> ligands, initially used Sb<sup>i</sup>Pr<sub>3</sub>, and was only later extended to phosphines and arsines.<sup>3</sup> The same group has also made significant contributions to organometallic Rh, Ir and Ru chemistry with Sb<sup>i</sup>Pr<sub>3</sub> and shown that these complexes exhibit different reactivity to the P<sup>i</sup>Pr<sub>3</sub> and As<sup>i</sup>Pr<sub>3</sub> species.<sup>4</sup> Also, the nickel- $SbPh_3$  complexes [Ni(2-methylallyl)( $SbPh_3$ )<sub>3</sub>][BARF] (BARF =  $[B\{C_6H_3-3,5-(CF_3)_2\}_4]^-)$  and *trans*- $[Ni(C_6Cl_2F_3)_2(SbPh_3)_2]$  are efficient catalysts for styrene polymerization and norbornene insertion polymerization respectively.5,6

Only a limited range of distibine ligands are known and none are available commercially. We have been interested in developing

synthetic methods for distibines and have used the reaction of R<sub>2</sub>SbCl with a variety of di-Grignard reagents to produce *m*- and *p*-phenylene and *o*-, *m*- and *p*-xylylene distibines in remarkably high yields.<sup>7</sup> Subsequently we have explored the ligating characteristics of these compounds towards a range of transition metal carbonyls and (mostly with *o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SbMe<sub>2</sub>)<sub>2</sub>) with transition metal halides.<sup>8</sup> The *o*-xylyl distibine turns out to be a versatile ligand capable of adjusting its chelate bite,  $d(Sb \cdots Sb)$ , by ~0.5 Å to accommodate the preferred geometry at the metal ion. Very recently we have begun to explore the chemistry of these and related distibines with organometallic reagents and have fully characterised the first examples of stable Pt(IV) stibine complexes, [PtMe<sub>3</sub>I(distibine)] and [(PtMe<sub>3</sub>)<sub>2</sub>( $\mu$ -R<sub>2</sub>SbCH<sub>2</sub>SbR<sub>2</sub>)] (R = Me or Ph) and shown that they undergo reductive elimination of ethane upon thermolysis.<sup>9</sup>

In this paper we describe the coordination of the distibute ligands  $Ph_2Sb(CH_2)_3SbPh_2$ ,  $Me_2Sb(CH_2)_3SbMe_2$  and  $o-C_6H_4(CH_2SbMe_2)_2$  with a range of Rh(1) and Ir(1) organometallic species, including their syntheses and spectroscopic properties and the crystal structure of [Rh(CO){Ph\_2Sb(CH\_2)\_3SbPh\_2}\_2]PF\_6. Some reaction chemistry of Rh(1) and Ir(1) complexes containing Ph\_2Sb(CH\_2)\_3SbPh\_2 is also described.

A number of Rh(1) complexes involving SbPh<sub>3</sub> have been described.<sup>1</sup> Specifically, the interaction of SbPh<sub>3</sub> with rhodium carbonyl halides has been studied by several groups,<sup>10-13</sup> and both the yellow, planar, four-coordinate *trans*-[Rh(CO)(SbPh<sub>3</sub>)<sub>2</sub>Cl] and the red, trigonal bipyramidal, five-coordinate [Rh(CO)(SbPh<sub>3</sub>)<sub>3</sub>Cl]

School of Chemistry, University of Southampton, Highfield, Southampton, UK SO17 1BJ. E-mail: gr@soton.ac.uk

have been structurally characterised,<sup>11</sup> as well as the planar  $[Rh(CO)(SbPh_3)_2I]$ .<sup>12</sup> The five-coordinate  $[Rh(CO)(SbPh_3)_3CI]$  undergoes oxidative addition with various substrates, including MeI which gives  $[Rh(CO)(SbPh_3)_2I_2(Me)]$ , whose structure shows *trans* stibines and *cis* iodines.<sup>11,13–15</sup>

SbPh<sub>3</sub> and  $[Rh(cod)Cl]_2$  are reported to give  $[Rh(SbPh_3)_2-(cod)Cl]$  as an orange solid on the basis of spectroscopic and analytical data.<sup>16</sup>  $[Rh(CO)_2Cl]_2$  also reacts with  $R_2SbCH_2SbR_2$  (R = Me or Ph) to give the ligand bridged dimers *trans*-[{Rh(CO)Cl}\_2(\mu-R\_2SbCH\_2SbR\_2)\_2].<sup>17,18</sup>

# **Results and discussion**

#### Rhodium(I)-cod-stibine systems

The previously reported  $[Rh(SbPh_3)_2(cod)Cl]^{16}$  was re-prepared by adding  $[Rh_2Cl_2(cod)_2]$  to a refluxing solution of excess SbPh\_3 in dry EtOH under argon. The reaction precipitated a red solid, in good yield. The formulation of the product as the  $1:2 Rh: SbPh_3$  species follows from microanalysis, integration of the resonances in the <sup>1</sup>H NMR spectrum and mass spectrometry, which exhibits a cluster of peaks centred at 917, corresponding to the  $[Rh(cod)(SbPh_3)_2]^+$  cation.

The five-coordinate 18-electron Rh(I) cod complexes incorporating distibute ligands,  $[Rh(cod){Ph_2Sb(CH_2)_3SbPh_2}Cl]$ and [Rh(cod){Me<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbMe<sub>2</sub>}Cl] were prepared by adding  $[Rh_2Cl_2(cod)_2]$  to a solution of the appropriate ligand (2 mol. equiv.) in dry EtOH under argon. The reaction mixtures were concentrated to dryness and triturated in hexane to afford orange precipitates in good yield. The <sup>1</sup>H NMR spectroscopic data for both of the complexes show the presence of cod and the distibine, and although the complexes appear to be fluxional at 300 K, at 223 K the <sup>1</sup>H NMR spectra show separate peaks (broad) for the distinct environments of the cod protons and the SbMe groups. The electrospray mass spectra exhibit mass peaks (with the correct isotope distributions) at 805 and 557 corresponding to the ions  $[Rh(cod){Ph_2Sb(CH_2)_3SbPh_2}]^+$ and  $[Rh(cod){Me_2Sb(CH_2)_3SbMe_2}]^+$  respectively. Conductivity measurements confirm that these are neutral, and hence 18electron, five-coordinate species. Attempts to obtain [Rh(cod){o- $C_6H_4(CH_2SbMe_2)_2$  Cl] similarly afforded a yellow orange solid, the electrospray mass spectrum of which revealed the [Rh(cod){o- $C_6H_4(CH_2SbMe_2)_2$ <sup>+</sup> cation as the only significant species. However, even after recrystallisation we were unable to obtain an analytically pure sample and the <sup>1</sup>H NMR spectrum was more complicated than expected, hence this species was not pursued. The five-coordinate Rh(I) distibine complexes described here are expected to have a distorted trigonal bipyramidal geometry similar to that observed for  $[Ir(C_2H_4)_2(Sb'Pr_3)_2Cl]$ , the crystal structure of which shows equatorial olefins and one axial and one equatorial stibine.4

The related planar 16-electron Rh(I) species  $[Rh(cod)(L-L)]BF_4$  (L–L =  $Ph_2Sb(CH_2)_3SbPh_2$ ,  $Me_2Sb(CH_2)_3SbMe_2$ ,  $o-C_6H_4(CH_2SbMe_2)_2$ ) were obtained in good yield as yellow orange solids through reaction of acetone solutions of  $[Rh_2Cl_2(cod)_2]$  with two mol. equiv. AgBF<sub>4</sub>, removal of the AgCl precipitate by filtration, and addition of a toluene solution of two mol. equiv. of L–L. The positive ion electrospray MS of the isolated species are indistinguishable from those of the neutral Rh(I) species above,

but these compounds are spectroscopically simpler, with <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra consistent with static, planar cations, and IR spectra revealing the ionic  $BF_4^-$  anion.

#### Rhodium(I)-bis(distibine) systems

In an effort to obtain [Rh(L-L)<sub>2</sub>]BF<sub>4</sub>, an acetone solution of  $[Rh_2Cl_2(cod)_2]$  was treated with two mol. equiv. AgBF<sub>4</sub>, filtered to remove the AgCl, and then 4.1 mol. equiv. of Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub> in toluene was added and the reaction mixture heated to 90 °C for ca. 1 h. However, spectroscopic analysis of the resulting yellow orange solid showed incomplete substitution of the cod ligand, giving  $[Rh(cod){Ph_2Sb(CH_2)_3SbPh_2}]BF_4$  as the major product, with the  $[Rh{Ph_2Sb(CH_2)_3SbPh_2}_2]BF_4$  as a minor product. This contrasts with the reaction chemistry of the analogous diphosphine ligands which readily produce [Rh(diphosphine)<sub>2</sub>]BF<sub>4</sub> via similar reactions even at room temperature.<sup>19,20</sup> The complex  $[Rh{Ph_2Sb(CH_2)_3SbPh_2}_2]BF_4$  was however obtained in good yield as a red solid from reaction of the more labile [Rh<sub>2</sub>Cl<sub>2</sub>(coe)<sub>4</sub>] with two mol. equiv. AgBF<sub>4</sub> in acetone, removal of the AgCl by filtration, and addition of the resulting yellow solution to a toluene solution of L-L at room temperature. The formulation follows from the positive ion electrospray MS which shows major peaks corresponding to  $[Rh{Ph_2Sb(CH_2)_3SbPh_2}_2]^+$  ([M]+) and loss of one SbPh<sub>2</sub> unit,  $[M - SbPh_2]^+$ , microanalysis, IR and <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy. Some reactions of this compound are described below. Attempts to obtain [Rh{o- $C_6H_4(CH_2SbMe_2)_2$ ]BF<sub>4</sub> both using the reaction conditions described for [Rh{Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}<sub>2</sub>]<sup>+</sup> or using TlPF<sub>6</sub> in place of AgBF<sub>4</sub> were not successful.

#### Rhodium(I)-carbonyl-stibine systems

The known [Rh(CO)(SbPh<sub>3</sub>)<sub>2</sub>Cl] was synthesised by reaction of [Rh<sub>2</sub>Cl<sub>2</sub>(CO)<sub>4</sub>] with 2 mol. equiv. of the appropriate ligand in dry CH<sub>2</sub>Cl<sub>2</sub>. The reaction was monitored by solution IR spectroscopy, and when the reaction was complete the solvent was removed *in vacuo* and the resulting material was triturated with hexane to give [Rh(CO)(SbPh<sub>3</sub>)<sub>2</sub>Cl] with <sup>1</sup>H NMR and IR spectroscopic data in line with the literature.<sup>11</sup> The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum shows a doublet due to the coordinated carbonyl at  $\delta$  184.3 ppm ( $J_{Rh-C} = 57$  Hz). Positive ion electrospray MS shows the major peaks centred at 837 corresponding to [Rh(CO)(SbPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>.

Reaction of [Rh<sub>2</sub>Cl<sub>2</sub>(CO)<sub>4</sub>] with 2 mol. equiv. of Ph<sub>2</sub>Sb-(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub> in dry, degassed CH<sub>2</sub>Cl<sub>2</sub> solution gives [Rh(CO)-{Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}<sub>2</sub>][Rh(CO)<sub>2</sub>Cl<sub>2</sub>] as an orange solid in good yield. The IR spectrum shows three v(CO) bands both in CH<sub>2</sub>Cl<sub>2</sub> solution and in the solid. The bands at 2068 (s) and 1989 (m)  $cm^{-1}$  $(CH_2Cl_2)$  correspond to the  $[Rh(CO)_2Cl_2]^-$  anion,<sup>22</sup> while the third band at 1968 (m) cm<sup>-1</sup> corresponds to the [Rh(CO){Ph<sub>2</sub>Sb-(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}<sub>2</sub>]<sup>+</sup> cation. The phosphine analogue, [Rh(CO)- $(dppp)_2$ <sup>+</sup> has  $v(CO) = 1930 \text{ cm}^{-1}$ , *i.e.* significantly to low frequency of the directly analogous distibine complex, and consistent with a more electron rich Rh centre in the phosphine.<sup>21</sup> The <sup>1</sup>H NMR spectrum shows coordinated ligand, while the  ${}^{13}C{}^{1}H$  NMR spectrum shows a doublet at  $\delta$  182.3 ppm ( $J_{\text{Rh-C}} = 71$  Hz) indicating the presence of the anion, but the carbonyl group on the cation was not evident, possibly due to fluxionality in the five-coordinate species. The most significant feature in the





Scheme 1 Summary of Rh chemistry.

positive ion electrospray MS is a cluster of peaks at *ca*. 1289 corresponding to  $[Rh{Ph_2Sb(CH_2)_3SbPh_2}_2]^+$  with loss of CO, with a much weaker feature (*ca*. 5%) corresponding to  $[Rh(CO){Ph_2Sb(CH_2)_3SbPh_2}_2]^+$ . The only significant feature in the negative ion electrospray MS is at 229 mass units, corresponding to the rhodium anion  $[Rh(CO)_2Cl_2]^-$ . The formulation was also confirmed by microanalysis.

The ionic [Rh(CO){Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}<sub>2</sub>][Rh(CO)<sub>2</sub>Cl<sub>2</sub>] species was subsequently treated with 2 mol. equiv. of Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub> in dry  $CH_2Cl_2$  and stirred under argon. This led to loss of  $\nu(CO)$ for the Rh(I) anion, leaving only the v(CO) band at 1966 cm<sup>-1</sup> for the  $[Rh(CO){Ph_2Sb(CH_2)_3SbPh_2}_2]^+$  cation. The presence of this species was further confirmed by positive ion electrospray MS. In another experiment  $[Rh(CO){Ph_2Sb(CH_2)_3SbPh_2}_2]$ [Rh(CO)<sub>2</sub>Cl<sub>2</sub>], 2 mol. equiv. of Ph<sub>2</sub>Sb(CH<sub>2</sub>)SbPh<sub>2</sub> and 2 mol. equiv. of NH<sub>4</sub>PF<sub>6</sub> were dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> and stirred at room temperature. The solution IR spectrum showed that the reaction was complete within 10 min, and the NH<sub>4</sub>Cl was filtered off. The orange solid was isolated by concentration of the reaction mixture and precipitation with Et<sub>2</sub>O. The <sup>1</sup>H NMR spectrum again showed coordinated ligand, and the positive ion electrospray MS and solution IR spectra were very similar to those above. The Nujol mull IR spectrum showed one v(CO) band at 1952 cm<sup>-1</sup>, with further bands at 837 and 557 cm<sup>-1</sup> confirming the presence of ionic PF<sub>6</sub><sup>-</sup>. Similar complexes with diphosphines have been reported previously, although these are typically obtained via bubbling CO into solutions of the planar 16-electron [Rh(diphosphine)<sub>2</sub>]<sup>+</sup> cations.19,20

Crystals of  $[Rh(CO){Ph_2Sb(CH_2)_3SbPh_2}_2]PF_6\cdot3/4CH_2Cl_2$ were obtained by layering a solution of the complex in CH<sub>2</sub>Cl<sub>2</sub> with hexane. The crystal structure shows two independent cations and anions in the asymmetric unit and two partially occupied CH<sub>2</sub>Cl<sub>2</sub> solvent molecules. The two Rh(I) cations are essentially indistinguishable (Fig. 1, Table 1), showing distorted five-coordinate, trigonal bipyramidal coordination environments based upon two chelating distibines and one CO ligand in an equatorial position. The Rh–Sb distances (2.54–2.62 Å) in this Rh(I) species compare with 2.594(2) and 2.611(2) Å in the

Table 1 Selected bond lengths (Å) and angles (°) for  $[Rh(CO){Ph_2Sb-(CH_2)_3SbPh_2}_2]PF_6\cdot3/4CH_2Cl_2$ 

Rh1–Sb1	2.5404(6)	Rh2–Sb5	2.5588(7)
Rh1–Sb2	2.5967(7)	Rh2–Sb6	2.6173(7)
Rh1–Sb3	2.6062(7)	Rh2–Sb7	2.5585(7)
Rh1–Sb4	2.5579(6)	Rh2–Sb8	2.6080(7)
Rh1-C55	1.875(7)	Rh2-C110	1.856(7)
Sb-C	2.119(7)-2.156(6)	Sb-C	2.116(6)-2.164(7)
C55–O1	1.141(8)	C110-O2	1.151(8)
C55-Rh1-Sb1	88.67(19)	C110-Rh2-Sb5	89.4(2)
C55-Rh1-Sb2	128.5(2)	C110-Rh2-Sb6	133.8(2)
C55-Rh1-Sb3	125.2(2)	C110-Rh2-Sb7	90.1(2)
C55-Rh1-Sb4	91.36(19)	C110-Rh2-Sb8	126.4(2)
Sb1-Rh1-Sb2	87.70(2)	Sb5-Rh2-Sb6	87.04(2)
Sb1-Rh1-Sb3	91.26(2)	Sb5-Rh2-Sb7	178.53(3)
Sb1-Rh1-Sb4	177.99(2)	Sb5-Rh2-Sb8	93.15(2)
Sb2-Rh1-Sb3	106.16(2)	Sb6-Rh2-Sb7	92.33(2)
Sb2-Rh1-Sb4	93.85(2)	Sb6-Rh2-Sb8	99.78(2)
Sb3-Rh1-Sb4	87.08(2)	Sb7-Rh2-Sb8	88.26(2)



Fig. 1 View of the structure of  $[Rh(CO){Ph_2Sb(CH_2)_3SbPh_2}_2]^*$  showing the Rh1 centred cation with numbering scheme adopted. The second cation in the structure is very similar. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Rh(III) cation *trans*-[RhCl<sub>2</sub>{Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}<sub>2</sub>]<sup>+.23</sup> The Rh–CO distances of 1.875(7) and 1.856(7) Å compare with d(Rh–CO) = 1.894(6) Å in [Rh(CO)(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>]<sup>+19</sup> and 1.886(4), 1.922(5) Å in [Rh<sub>2</sub>(CO)<sub>4</sub>{Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub>}<sub>3</sub>]<sup>2+.20</sup>

Under similar reaction conditions, treatment of [Rh<sub>2</sub>Cl<sub>2</sub>(CO)<sub>4</sub>] with four mol. equiv. of Me<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbMe<sub>2</sub> or o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>- $SbMe_2$  in dry  $CH_2Cl_2$  solution leads to the formation of dark brown materials over the period of a few minutes, with substantial decomposition. No well-defined product was obtained from this reaction (it has been noted previously that other rhodium(I) complexes involving distibinomethanes also decompose readily even in the solid state).<sup>18</sup> However, repeating the reaction using a 1 : 2 molar ratio of [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> : Me<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbMe<sub>2</sub> in  $CH_2Cl_2$  solution at *ca*. -15 °C for  $\sim 30$  min afforded the compound  $[Rh(CO){Me_2Sb(CH_2)_3SbMe_2}_2][Rh(CO)_2Cl_2]$  as a dark red solid, as shown by electrospray mass spectrometry, IR, <sup>1</sup>H and <sup>13</sup>C $\{^{1}H\}$ NMR spectroscopy and microanalysis. In contrast to the Rhcarbonyl complex of the Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub> analogue above, this methyl-substituted ligand complex decomposes significantly in solution at RT over a period of minutes, hence spectra were recorded at -30 °C. Treatment of this complex with excess distibine or addition of PF<sub>6</sub><sup>-</sup> did not result in complete replacement of the  $[Rh(CO)_2Cl_2]^-$  anion.

The corresponding  $[Rh(CO){o-C_6H_4(CH_2SbMe_2)_2}]$  $(CO)_2Cl_2$ ] was obtained similarly, but decomposes very readily in solution. [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> reacts with four mol. equiv. of Ph<sub>2</sub>SbCH<sub>2</sub>-SbPh<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> to form the known dimer<sup>18</sup> [Rh<sub>2</sub>(CO)<sub>2</sub>Cl<sub>2</sub>- ${Ph_2SbCH_2SbPh_2}_2$  initially ( $v_{CO} = 2000 \text{ cm}^{-1}$ ). With continued stirring at RT the reaction proceeds to afford another CO containing species ( $v_{\rm CO} = 1970 \text{ cm}^{-1}$ ), which may be a cationic Rh(I) carbonyl, but even in the presence of  $NH_4PF_6$  the reaction is incomplete and a substantial amount of the dimer remains. The positive ion electrospray MS supports these conclusions, revealing peaks at m/z 1429 ([Rh<sub>2</sub>(CO)<sub>2</sub>Cl{Ph<sub>2</sub>SbCH<sub>2</sub>SbPh<sub>2</sub>}<sub>2</sub>]<sup>+</sup>) and m/z 1263 ([Rh(CO){Ph<sub>2</sub>SbCH<sub>2</sub>SbPh<sub>2</sub>}]<sup>+</sup>); however, we were unable to isolate an analytically pure sample, and given that distibinomethanes show a much lower tendency to chelate compared to diphosphinomethanes, this was not pursued.

#### Rhodium(I) reaction chemistry

Our investigations of the reaction chemistry have focused on the Rh(I) complexes with  $Ph_2Sb(CH_2)_3SbPh_2$ , since these were found to be more stable both in the solid and in solution compared to the methyl-substituted distibute complexes.

Bubbling CO through a solution of  $[Rh{Ph_2Sb(CH_2)_3SbPh_2}_2]$ -BF<sub>4</sub> in acetone leads initially to the appearance of a single v(CO) band at 1966 cm<sup>-1</sup>, due to the monocarbonyl cation [Rh-(CO){Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}<sub>2</sub>]<sup>+</sup>, providing an alternative synthesis for this complex. Continued exposure to a CO atmosphere over a period of ca. 1 h leads to this CO absorption band being replaced by two new bands at 2020 and 1993 cm<sup>-1</sup>, consistent with a cis-dicarbonyl Rh(I) complex. This species is unstable in the absence of a CO atmosphere, reverting fully to [Rh(CO)- $\{Ph_2Sb(CH_2)_3SbPh_2\}_2^{\dagger}$ . The formation of the dicarbonyl complex from the 18-electron monocarbonyl cation could occur via either dissociation of a distibine (to give [Rh(CO)<sub>2</sub>{Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>-SbPh<sub>2</sub>}]<sup>+</sup> and free distibine) or via reversible chelate ring opening (to give the five-coordinate  $[Rh(CO)_2 \{Ph_2Sb(CH_2)_3SbPh_2\} \{\kappa^1 Sb-$ Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}]<sup>+</sup>). For comparison, the 16-electron planar  $cis[Rh(CO)_{2}{Ph_{2}P(CH_{2})_{2}PPh_{2}}]^{+}$  gives v(CO) = 2100 and 2055 cm<sup>-1</sup>,<sup>24</sup> while the dimeric five-coordinate Rh(I) dicarbonyl complex [{(CO)<sub>2</sub>{Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub>}Rh}<sub>2</sub>{ $\mu$ -Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub>}] gives v(CO) = 2020 and 1965 cm<sup>-1</sup>.<sup>20</sup> Both on the basis of the CO stretching frequencies and the observation that the distibine complex converts reversibly to  $[Rh(CO){Ph_2Sb(CH_2)_3SbPh_2}_2]^+$ , it seems more likely that the cis-dicarbonyl complex is the fivecoordinate  $[Rh(CO)_2 \{Ph_2Sb(CH_2)_3SbPh_2\} \{\kappa^1Sb-Ph_2Sb(CH_2)_3 SbPh_2$ ]<sup>+</sup>, although we have not been able to obtain crystals to prove this unequivocally. Furthermore, Hieber and Frey have described the five-coordinate dicarbonyl stibine complex  $[Rh(CO)_2(SbPh_3)_3][AlCl_4]$  which has  $v(CO) = 2009 \text{ cm}^{-1} (KBr).^{25}$ 

In CH<sub>2</sub>Cl<sub>2</sub> solution  $[Rh(CO){Ph_2Sb(CH_2)_3SbPh_2}_2]PF_6$  undergoes oxidative addition with Br<sub>2</sub> to give the known Rh(III) complex cation *trans*- $[RhBr_2{Ph_2Sb(CH_2)_3SbPh_2}_2]^+$  (IR, MS and NMR evidence).<sup>23</sup> However, no reaction was apparent when either  $[Rh(CO){Ph_2Sb(CH_2)_3SbPh_2}_2]PF_6$  or  $[Rh{Ph_2Sb(CH_2)_3SbPh_2}_2]BF_4$  were heated with MeI.

Treatment of a CH<sub>2</sub>Cl<sub>2</sub> solution of [Rh(CO){Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>-SbPh<sub>2</sub>}<sub>2</sub>]PF<sub>6</sub> with excess HCl saturated CH<sub>2</sub>Cl<sub>2</sub> solution leads to loss of the band due to the CO stretching vibration in the IR spectrum. Spectroscopic analysis of the product obtained after removal of the CH<sub>2</sub>Cl<sub>2</sub> shows that there is a mixture of products, one of which was identified by <sup>1</sup>H NMR spectroscopy as a Rh(III)-hydride, giving  $\delta$  –18.95 ppm, <sup>1</sup>J<sub>RhH</sub> = 7.2 Hz. We tentatively assign this to the neutral [RhHCl<sub>2</sub>{Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}] by comparison of the spectroscopic data with those for the five-coordinate [RhHCl<sub>2</sub>(SbPh<sub>3</sub>)<sub>2</sub>] $(\delta$ <sup>1</sup>H = –18.3, <sup>1</sup>J<sub>RhH</sub> = 7 Hz) reported by Mague and Wilkinson.<sup>26</sup>

We were also able to grow a few small crystals of a second species from a solution of the products in CHCl<sub>3</sub> over a few days. The crystal structure† shows (Fig. 2) a very unexpected Rh(III) species of formula [RhCl<sub>2</sub>{Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}-{PhClSb(CH<sub>2</sub>)<sub>3</sub>SbClPh}]Cl·CHCl<sub>3</sub>. The Rh atom is surrounded

<sup>&</sup>lt;sup>†</sup> The crystallographic data for this compound were rather weak, giving higher than normal residuals. Hence detailed comparisons of geometric parameters require caution.



**Fig. 2** View of the structure of  $[RhCl_{2}{Ph_{2}Sb(CH_{2})_{3}SbPh_{2}}{PhClSb-(CH_{2})_{3}SbClPh}]Cl with atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Rh1–Cl2 = 2.371(3), Rh1–Cl1 = 2.410(3), Rh1–Sb1 = 2.5896(13), Rh1–Sb2 = 2.5920(14), Rh1–Sb4 = 2.6045(14), Rh1–Sb3 = 2.6261(13), Sb3–Cl3 = 2.440(3), Sb3···Cl5 = 2.736(3), Sb4–Cl4 = 2.435(4), Sb4···Cl5 = 2.823(3) Å; Cl2–Rh1–Cl1 = 174.86(11), Sb1–Rh1–Sb2 = 89.56(4), Sb1–Rh1–Sb4 = 97.75(5), Sb2–Rh1–Sb4 = 170.86(5), Sb1–Rh1–Sb3 = 176.92(5), Sb2–Rh1–Sb3 = 91.09(4), Sb4–Rh1–Sb3 = 81.90(4), Sb3···Cl5···Sb4 = 76.13(8).$ 

by two *trans* Cl's and four Sb atoms, two from a chelating  $Ph_2Sb(CH_2)_3SbPh_2$  (d(Rh-Sb) = 2.590(1), 2.592(1) Å) and two from a bis(phenylchlorostibino)propane, (d(Rh-Sb) = 2.604(1), 2.626(1) Å). A Cl<sup>-</sup> anion is also present to provide charge balance, and this is involved in long range bridging secondary interactions with the two Sb atoms of the modified ligand,  $d(Sb \cdots Cl) = 2.736(3)$ , 2.823(3) Å, Sb  $\cdots$  Cl  $\cdots$  Sb = 76.13(8)°. Thus, it is clear that one of the Ph ring substituents on each Sb atom of one ligand has undergone cleavage with HCl, being replaced by a Cl atom. The crystal data were weak and hence the final residuals are rather high, precluding detailed comparisons of the parameters.

Secondary Sb...Cl interactions are well known in antimony chloride anions, however, structural data on examples involving  $R_2$ SbCl units (as presented here) are very rare. A survey of the Cambridge Crystallographic Database shows that the Sb...Cl distances in the Rh complex described here lie at the short end of the normal bond length range for secondary interactions in chloroantimony anions, with values between 2.9 and 3.2 Å being more typical, *e.g.* in [Sb<sub>2</sub>Cl<sub>6</sub>{*o*-C<sub>6</sub>H<sub>4</sub>(AsMe<sub>2</sub>)<sub>2</sub>]] *d*(Sb...Cl) = 3.020(3), 3.171(2), 3.267(3) Å.<sup>27</sup> The unusually short Sb...Cl distances in this species could be a consequence of (i) the geometric constraints imposed by the coordination of the Sb atoms to Rh, (ii) the presence of the C<sub>3</sub>-unit linking the Sb atoms and (iii) the metal coordination which will make the Sb atoms less electron rich and hence promote stronger Sb...Cl interactions.

It is known that phenylstibines can undergo cleavage with HCl gas to give chlorostibines (indeed we have used this reaction regularly to prepare the distibine ligands in this work), however, the chlorostibines are not generally considered as ligands for metal centres, and in fact the Rh(III) complex reported here is the first structurally characterized example of a metal coordinated to a chlorostibine. We do not know whether the Ph cleavage occurs while the distibine is coordinated to rhodium, but the chlorostibine produced clearly behaves as a ligand in the isolated Rh(III) species. This reaction chemistry is different from that of phenylphosphines, which do not undergo P–Ph cleavage by HCl.

The planar 16-electron  $[Rh{Ph_2Sb(CH_2)_3SbPh_2}_2]BF_4$  was also treated with HCl saturated acetone, and the same Rh–hydride product ( $\delta^1 H = -18.95$ , J = 7.2 Hz) was identified from *in situ* <sup>1</sup>H NMR studies. A very weak feature in the IR spectrum at 1998 cm<sup>-1</sup> is tentatively assigned to the Rh–H stretching vibration.

#### Iridium(I)-stibine complexes

Few examples of iridium(I) stibine complexes are known, and none involve distibine coordination.1 The solution obtained by treatment of [Ir<sub>2</sub>(cod)<sub>2</sub>Cl<sub>2</sub>] with two mol. equiv. of AgBF<sub>4</sub> in acetone (following filtration to remove the AgCl) reacts with two mol. equiv. of L-L  $(L-L = Ph_2Sb(CH_2)_3SbPh_2$  or  $o-C_6H_4(CH_2SbMe_2)_2$ ) to give the planar, 16-electron species  $[Ir(cod)(L-L)]BF_4$  in an analogous manner to the Rh chemistry described above. The identity of the light orange products follow from positive ion electrospray MS, IR, <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy and microanalysis. Using  $[Ir_2(coe)_4Cl_2]$  and AgBF<sub>4</sub> in acetone, followed by addition of a toluene solution of Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub> produces an orange solution from which the planar Ir(I) species  $[Ir{Ph_2Sb(CH_2)_3SbPh_2}_2]BF_4$  may be obtained in good yield. NMR spectroscopy reveals adventitious CH<sub>2</sub>Cl<sub>2</sub> in this sample. Bubbling CO gas through an acetone solution of  $[Ir{Ph_2Sb(CH_2)_3SbPh_2}_2]BF_4$  leads to the appearance of two strong IR bands at 2018 and 1996 cm<sup>-1</sup> attributed to a dicarbonyl complex. The positive ion ES MS of this solution shows peaks at m/z = 1435 and 1407 assigned to  $[Ir(CO)_2 \{Ph_2Sb(CH_2)_3SbPh_2\}_2]^+$ and  $[Ir(CO){Ph_2Sb(CH_2)_3SbPh_2}_2]^+$ . The CO is lost on pumping the solution to dryness in vacuo.

# Conclusions

These results show that a range of four- and five-coordinate Rh(I) and Ir(I) distibine complexes involving various organometallic co-ligands may be obtained through careful choice of the metal precursor and the reaction conditions. The complexes of Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub> appear to be the most stable, presumably the coordinated –SbPh<sub>2</sub> units lead to less electron-rich, and hence less reactive, complexes compared to the coordinated -SbMe<sub>2</sub> units, which appear to undergo Sb-C fission in some of the reactions.  $[Rh(CO){Ph_2Sb(CH_2)_3SbPh_2}_2]PF_6$  and  $[Rh{Ph_2Sb(CH_2)_3}$ -SbPh<sub>2</sub>}<sub>2</sub>]BF<sub>4</sub> undergo oxidative addition with Br<sub>2</sub> and HCl. The reaction with HCl also yields the very unexpected trans- $[RhCl_{2}{Ph_{2}Sb(CH_{2})_{3}SbPh_{2}}{PhClSb(CH_{2})_{3}SbClPh}]Cl, which$ represents the first structurally characterised example of a coordinated chlorostibine. Work is underway in our laboratories to investigate the reactions of organoantimony chlorides with transition metals.

## Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer 983G spectrometer over the range 4000– 200 cm<sup>-1</sup>, or in chlorocarbon solution over the range 2300– 1700 cm<sup>-1</sup>. Mass spectra were run by positive ion or negative ion electrospray (MeCN solution) using a VG Biotech platform. <sup>1</sup>H NMR spectra were recorded using a Bruker AV300 spectrometer. <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded using a Bruker DPX400 spectrometer operating at 100.6 MHz and are referenced to TMS. 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> or Ar atmosphere. Percentage yields are based upon the metal. The Rh(I) and Ir(I) precursors [Rh<sub>2</sub>Cl<sub>2</sub>(CO)<sub>4</sub>],<sup>28</sup> [M<sub>2</sub>Cl<sub>2</sub>(cod)<sub>2</sub>],<sup>29,30</sup> [M<sub>2</sub>Cl<sub>2</sub>(coe)<sub>4</sub>] (M = Rh or Ir)<sup>31</sup> and the ligands were prepared as described previously.<sup>7,32,33</sup>

#### Rhodium(I) compounds

**[Rh(cod)(SbPh<sub>3</sub>)<sub>2</sub>Cl].** [Rh<sub>2</sub>Cl<sub>2</sub>(cod)<sub>2</sub>] (0.049 g, 0.10 mmol) was added to a refluxing solution of SbPh<sub>3</sub> (1.0 g, 2.9 mmol) in dry EtOH (10 mL) under argon. An orange precipitate formed immediately, was filtered off, washed with CH<sub>2</sub>Cl<sub>2</sub>/hexane and dried *in vacuo*. Yield 0.2 g, 100%. Required for [C<sub>44</sub>H<sub>42</sub>ClRhSb<sub>2</sub>]·1/2CH<sub>2</sub>Cl<sub>2</sub>: C, 53.7; H, 4.4%. Found: C, 53.7; H, 3.8%. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 300 K): δ 7.50–7.30 (m) [30H] (Ph), 5.43 (s) CH<sub>2</sub>Cl<sub>2</sub>, 4.25 (br) [4H] (cod CH), 2.45 (m) [4H] (cod CH<sub>2</sub>), 1.85 (br) [4H] (cod CH<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 225 K): δ 136.3 (s), 135.7 (s), 134.8 (s), 129.1 (s), 128.8 (s) (Ph), 78.0 (d) J = 15 Hz (cod CH) (cod CH<sub>2</sub> resonances obscured by solvent) ppm. ES<sup>+</sup> MS (MeCN): *m/z* 563 [Rh(cod)(SbPh<sub>3</sub>)]<sup>+</sup>, 841 [Rh(SbPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>, 917 [Rh(cod)(SbPh<sub>3</sub>)]<sup>+</sup>.

[Rh(cod){Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}Cl]. Reaction as above using [Rh<sub>2</sub>Cl<sub>2</sub>(cod)<sub>2</sub>] (0.062 g, 0.126 mmol) and Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub> (0.15 g, 0.25 mmol). The deep orange solution was reduced to dryness and stirred in dry hexane until a precipitate formed. The orange solid was filtered off and dried *in vacuo*. Yield 0.093 g, 44%. Required for [C<sub>35</sub>H<sub>38</sub>ClRhSb<sub>2</sub>]·CH<sub>2</sub>Cl<sub>2</sub>: C, 46.7; H, 4.4%. Found: C, 47.4; H, 4.1%. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 300 K): δ 7.60– 7.20 (m) [20H] (Ph), 5.43 (s) CH<sub>2</sub>Cl<sub>2</sub>, 4.20 (br) [4H] (cod CH), 2.43 (br) [4H] (cod CH<sub>2</sub>), 2.33 (br) [6H] (CH<sub>2</sub>), 1.78 (br) [4H] (cod CH<sub>2</sub>) ppm. ES<sup>+</sup> MS (MeCN): *m/z* 805 [Rh(cod){Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>]<sup>+</sup>. Conductivity  $A_M/\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> (10<sup>-3</sup> mol dm<sup>-3</sup> in CH<sub>2</sub>Cl<sub>2</sub>): 4.68.

[Rh(cod){Me<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbMe<sub>2</sub>}Cl]. Reaction as above, except at room temperature using [Rh<sub>2</sub>Cl<sub>2</sub>(cod)<sub>2</sub>] and Me<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>-SbMe<sub>2</sub>. The orange precipitate was dried *in vacuo*. Yield 46%. Required for [C<sub>15</sub>H<sub>30</sub>ClRhSb<sub>2</sub>]·2CH<sub>2</sub>Cl<sub>2</sub>: C, 26.8; H, 4.5%. Found: C, 27.2; H, 5.0%. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO): δ 5.43 (s) CH<sub>2</sub>Cl<sub>2</sub>, 4.18 (br) [4H] (cod CH), 2.43 (br) [4H] (cod CH<sub>2</sub>), 2.32 (br) [6H] (CH<sub>2</sub>), 1.76 (br) [4H] (cod CH<sub>2</sub>), 1.35–1.20 (m) [12H] (SbMe) ppm. ES<sup>+</sup> MS (MeCN): *m/z* 557 [Rh(cod){Me<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbMe<sub>2</sub>}]<sup>+</sup>. Conductivity  $\Lambda_M/\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> (10<sup>-3</sup> mol dm<sup>-3</sup> in CH<sub>2</sub>Cl<sub>2</sub>): 2.25.

[Rh(cod){o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SbMe<sub>2</sub>)<sub>2</sub>}Cl]. Prepared at room temperature as above using [Rh<sub>2</sub>Cl<sub>2</sub>(cod)<sub>2</sub>] and o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SbMe<sub>2</sub>)<sub>2</sub>. Orange solid. Yield 40%. ES<sup>+</sup> MS (MeCN): m/z 619 [Rh(cod){o-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SbMe<sub>2</sub>)<sub>2</sub>]<sup>+</sup>. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  7.0–7.4 (m) [4H] (o-C<sub>6</sub>H<sub>4</sub>), 4.18 (br) [4H] (cod CH), 2.40 (br) [4H] (cod CH<sub>2</sub>), 2.32 (br) [6H] (CH<sub>2</sub>), 1.75 (br) [4H] (cod CH<sub>2</sub>), 1.30, 1.40 (m) [12H] (SbMe) ppm.

 $[Rh(cod){Ph_2Sb(CH_2)_3SbPh_2}]BF_4$ .  $[Rh_2Cl_2(cod)_2]$  (0.047 g, 0.095 mmol) and AgBF<sub>4</sub> (0.043 g, 0.22 mmol) were dissolved in degassed acetone (20 mL) and heated to reflux for 30 min, where upon a white precipitate formed. The yellow solution was

filtered and added dropwise to a solution of Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub> (0.225 g, 0.38 mmol) in degassed toluene (15 mL). The resulting orange solution was stirred at room temperature for *ca*. 1 h and then reduced to dryness *in vacuo*. The residues were recrystallised in CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to give a yellow/orange solid, which was filtered off and dried *in vacuo*. Yield 0.12 g, 74%. Required for [C<sub>35</sub>H<sub>38</sub>BF<sub>4</sub>RhSb<sub>2</sub>]: C, 47.1; H, 4.3%. Found: C, 47.0; H, 4.1%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.9–7.6 (m) [20H] (Ph), 4.2 (br) [4H] (cod CH), 2.3–2.5 (br) [14H] (CH<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  128.22–133.40 (Ph), 80.98 (cod CH), 31.48 (cod CH<sub>2</sub>), 17.36, 17.15 (CH<sub>2</sub>) ppm. ES<sup>+</sup> MS (MeCN): *m/z* 805 [Rh(cod){Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}]<sup>+</sup>. IR (Nujol mull): 1054 (BF<sub>4</sub><sup>-</sup>) cm<sup>-1</sup>.

[Rh(cod){Me<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbMe<sub>2</sub>}]BF<sub>4</sub>. Method as above using [Rh<sub>2</sub>Cl<sub>2</sub>(cod)<sub>2</sub>], AgBF<sub>4</sub> and Me<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbMe<sub>2</sub>. The product was recrystallised from Me<sub>2</sub>CO and Et<sub>2</sub>O. Yield 56%. Required for [C<sub>15</sub>H<sub>30</sub>BF<sub>4</sub>RhSb<sub>2</sub>]· $\frac{1}{4}$ toluene: C, 30.2; H, 4.8. Found: C, 30.1; H, 4.5%. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO): δ 4.0 (s) [4H] (cod CH), 2.4 (s) [8H] (cod CH<sub>2</sub>), 2.1–2.4 (br) [6H] (CH<sub>2</sub>), 1.7 (br) (12H) (SbMe) ppm (signals due to associated toluene solvent are also evident). <sup>13</sup>C{<sup>1</sup>H} NMR ((CD<sub>3</sub>)<sub>2</sub>CO): δ 79.31 (d 15 Hz) (cod CH), 31.45 (cod CH<sub>2</sub>), 23.94 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 18.75 (SbCH<sub>2</sub>), -6.00 (SbMe) ppm. ES<sup>+</sup> MS (MeCN): m/z 557 [Rh(cod){Me<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbMe<sub>2</sub>}]<sup>+</sup>. IR (Nujol mull): 1054 (BF<sub>4</sub><sup>-</sup>) cm<sup>-1</sup>.

 $[Rh{Ph_2Sb(CH_2)_3SbPh_2}_2]BF_4.$   $[Rh_2Cl_2(coe)_4]$ (0.064 0.09 mmol) and AgBF<sub>4</sub> (0.043 g, 0.22 mmol) were dissolved in degassed acetone (10 mL) and stirred for 45 min at RT, where upon a white precipitate formed. After filtering, the orange solution was added drop-wise to a solution of Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub> (0.225 g, 0.38 mmol) in degassed toluene (15 mL). The deep red solution was left to stir for 30 min, and reduced to dryness. The residues were dissolved in minimum acetone, and Et<sub>2</sub>O (10 mL) was added to precipitate a solid. The red solid was filtered off and dried in vacuo. Yield 0.2 g, 81%. Required for [C54H52BF4RhSb4]·CH2Cl2: C, 45.2; H, 3.7. Found: C, 45.4; H, 3.9%. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO): δ 6.8–7.5 (m) [40H] (Ph), 5.43 (s) CH<sub>2</sub>Cl<sub>2</sub>, 2.3–2.7 (br) [12H] (CH<sub>2</sub>) ppm (CH<sub>2</sub>Cl<sub>2</sub> solvent is also evident). <sup>13</sup>C{<sup>1</sup>H} NMR ((CD<sub>3</sub>)<sub>2</sub>CO): δ 129.42–137.07 (Ph), 24.71 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 21.62 (SbCH<sub>2</sub>) ppm. ES<sup>+</sup> MS (MeCN): m/z 1291  $[Rh{Ph_2Sb(CH_2)_3SbPh_2}_2]^+$ , 1013  $[Rh{Ph_2Sb(CH_2)_3SbPh_2}_2 SbPh_{2}^{+}$ . IR (Nujol mull): 1064 ( $BF_{4}^{-}$ ) cm<sup>-1</sup>.

**[Rh(CO)(SbPh<sub>3</sub>)<sub>2</sub>Cl].** [Rh<sub>2</sub>Cl<sub>2</sub>(CO)<sub>4</sub>] (0.082 g, 0.21 mmol) and SbPh<sub>3</sub> (0.30 g, 0.92 mmol) were dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and stirred for 2 h. The reaction was monitored by solution IR spectroscopy, and the reaction mixture was reduced to dryness and the residues were stirred in dry hexane (30 mL) until a dark red precipitate was formed. This was filtered off and the red solid was dried *in vacuo*. Yield 0.2 g, 100%. Required for [C<sub>37</sub>H<sub>30</sub>ClORhSb<sub>2</sub>]: C, 50.9; H, 3.5. Found: C, 50.6; H, 3.1%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ 7.90–7.30 (m) [30H] (Ph) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  184.3 (d) J = 57 Hz (CO), 134.9, 130.7, 128.9, 127.9 (Ph) ppm. ES<sup>+</sup> MS (MeCN): m/z 837 [Rh(CO)(SbPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. IR (CH<sub>2</sub>Cl<sub>2</sub>): 1967 (s) (CO) cm<sup>-1</sup>. IR (Nujol mull): 1952 (s) (CO) cm<sup>-1</sup>. Conductivity  $\Lambda_{\rm M}/\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> (10<sup>-3</sup> mol dm<sup>-3</sup> in CH<sub>2</sub>Cl<sub>2</sub>): 0.

[**Rh(CO)**{**Ph**<sub>2</sub>**Sb(CH**<sub>2</sub>)<sub>3</sub>**SbPh**<sub>2</sub>}<sub>2</sub>][**Rh(CO)**<sub>2</sub>**Cl**<sub>2</sub>]. Reaction as above with [Rh<sub>2</sub>Cl<sub>2</sub>(CO)<sub>4</sub>] (0.049 g, 0.126 mmol) and Ph<sub>2</sub>Sb-(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub> (0.15 g, 0.25 mmol). The orange precipitate was dried *in vacuo*. Yield 0.13 g, 68%. Required for [C<sub>57</sub>H<sub>52</sub>Cl<sub>2</sub>O<sub>3</sub>-Rh<sub>2</sub>Sb<sub>4</sub>]: C, 44.2; H, 3.3. Found: C, 43.4; H, 3.0%. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  7.60–7.40 (m) [20H] (Ph), 2.85 (bs) [4H] (CH<sub>2</sub>Sb), 2.05 (s) [2H] (CH<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  182.3 (d 71 Hz) ([Rh(CO)<sub>2</sub>Cl<sub>2</sub>]<sup>-</sup>), 136.1, 134.7, 131.2, 129.9 (Ph), 23.7 (CH<sub>2</sub>), 18.9 (CH<sub>2</sub>Sb) ppm. ES<sup>+</sup> MS (MeCN): *m/z* 1289 [Rh-{Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}<sub>2</sub>]<sup>+</sup>, 1317 [Rh(CO){Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}<sub>2</sub>]<sup>+</sup>. ES<sup>-</sup> MS (MeCN): *m/z* 229 [Rh(CO)<sub>2</sub>Cl<sub>2</sub>]<sup>-</sup>. IR (CH<sub>2</sub>Cl<sub>2</sub>): 2068 (s), 1989 (m), 1968 (m) (CO) cm<sup>-1</sup>. IR (Nujol mull): 2058 (s), 1977 (s), 1953 (s) (CO) cm<sup>-1</sup>.

 $\label{eq:response} \begin{array}{ll} [Rh(CO) \{Ph_2Sb(CH_2)_3SbPh_2\}_2]Cl. & A further two mol. equivalents of Ph_2Sb(CH_2)_3SbPh_2 were added to the [Rh(CO) {Ph_2-Sb(CH_2)_3SbPh_2}_2][Rh(CO)_2Cl_2] prepared above, in dry CH_2Cl_2, and the reaction was stirred under argon for 12 h and the progress was monitored by solution IR spectroscopy. An orange solid was isolated. IR (CH_2Cl_2): 1966 (s) (CO) cm^{-1}. ES^+ MS (MeCN): m/z 1289 [Rh{Ph_2Sb(CH_2)_3SbPh_2}_2]^+, 1317 [Rh(CO) {Ph_2Sb(CH_2)_3SbPh_2}_2]^+. \end{array}$ 

[Rh(CO){Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}<sub>2</sub>]PF<sub>6</sub>. [Rh(CO){Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>-SbPh<sub>2</sub>}<sub>2</sub>][Rh(CO)<sub>2</sub>Cl<sub>2</sub>] (0.067 g, 0.043 mmol), Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub> (0.051 g, 0.0865 mmol) and NH<sub>4</sub>PF<sub>6</sub> (0.016 g, 0.0865 mmol) were dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL). Solution IR spectroscopy indicated that the reaction was complete after 5 min. The fine white precipitate (NH<sub>4</sub>Cl) was removed by filtration and the resultant orange solution was concentrated to *ca*. 1 mL. Et<sub>2</sub>O (10 mL) was added to precipitate an orange solid, which was isolated by filtration and dried *in vacuo*. Yield 60%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.40–7.05 (m) [20H] (Ph), 1.90 (bs) [2H] (CH<sub>2</sub>CH<sub>2</sub>), 1.80 (bs) [4H] (CH<sub>2</sub>Sb) ppm. ES<sup>+</sup> MS (MeCN): *m/z* 1291 [Rh{Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}<sub>2</sub>]<sup>+</sup>, 1317 [Rh(CO){Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>-SbPh<sub>2</sub>}<sub>2</sub>]<sup>+</sup>. IR (CH<sub>2</sub>Cl<sub>2</sub>): 1967 (s) (CO) cm<sup>-1</sup>. IR (Nujol mull): 1952 (s) (CO), 837 (s) v(PF<sub>6</sub><sup>-</sup>), 557 (s)  $\delta$ (PF<sub>6</sub><sup>-</sup>) cm<sup>-1</sup>.

[Rh(CO){Me<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbMe<sub>2</sub>}<sub>2</sub>][Rh(CO)<sub>2</sub>Cl<sub>2</sub>]. Method as for [Rh(CO){Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}<sub>2</sub>][Rh(CO)<sub>2</sub>Cl<sub>2</sub>] above, except the solutions were maintained at ~ -15 °C with an ice–salt bath. Orange/brown solid. Yield 50%. Required for [C<sub>17</sub>H<sub>36</sub>Cl<sub>2</sub>O<sub>3</sub>-Rh<sub>2</sub>Sb<sub>4</sub>]: C, 19.4; H, 3.5; found: C, 20.2; H, 3.6%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.8–1.3 (br)[6H] (CH<sub>2</sub>), 1.22 (s) [12H] (SbMe). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 250 K):  $\delta$  193.0 (d 65 Hz) [Rh(CO){Me<sub>2</sub>Sb-(CH<sub>2</sub>)<sub>3</sub>SbMe<sub>2</sub>}<sub>2</sub>]<sup>+</sup>, 181.7 (d 79 Hz) ([Rh(CO)<sub>2</sub>Cl<sub>2</sub>]<sup>-</sup>), 23.04 (CH<sub>2</sub>), 16.89 (CH<sub>2</sub>), -0.16 (SbMe). ES<sup>+</sup> MS (MeCN): *m/z* 865 [Rh(CO){Me<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbMe<sub>2</sub>}<sub>2</sub>.MeCN]<sup>+</sup>, 795 [Rh{Me<sub>2</sub>Sb-(CH<sub>2</sub>)<sub>3</sub>SbMe<sub>2</sub>}<sub>2</sub>]<sup>+</sup>, 641 [Rh{Me<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbMe<sub>2</sub>}<sub>2</sub> - SbMe<sub>2</sub>]<sup>+</sup>. IR (CH<sub>2</sub>Cl<sub>2</sub>): 2069, 1988, 1966 (CO) cm<sup>-1</sup>. IR (Nujol mull): 2047 (sh), 1953 (v br) (CO) cm<sup>-1</sup>.

[Rh(CO){ $o-C_6H_4(CH_2SbMe_2)_2$ ][Rh(CO)<sub>2</sub>Cl<sub>2</sub>]. Method as above using [Rh<sub>2</sub>Cl<sub>2</sub>(CO)<sub>4</sub>] and  $o-C_6H_4(CH_2SbMe_2)_2$ . Orange/ brown solid. Yield 55%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 210 K):  $\delta$  7.0–7.5 (m) [8H] ( $o-C_6H_4$ ), 3.3–3.5 (m) [8H] (CH<sub>2</sub>), 1.15–1.22 (m) [24H] (SbMe). ES<sup>+</sup> MS (MeCN): found m/z = 947 [Rh(CO){ $o-C_6H_4(CH_2SbMe_2)_2$ }<sub>2</sub>]<sup>+</sup>. ES<sup>-</sup> MS (MeCN): found m/z = 229 [Rh(CO)<sub>2</sub>Cl<sub>2</sub>]<sup>-</sup>. IR (Nujol mull): 2075, 2007 (v br), 1974 (sh) (CO) cm<sup>-1</sup>.

## Iridium(I) compounds

 $[Ir(cod){Ph_2Sb(CH_2)_3SbPh_2}]BF_4$ .  $[Ir_2Cl_2(cod)_2]$  (0.0806 g, 0.12 mmol) and AgBF<sub>4</sub> (0.0493 g, 0.253 mmol) were dissolved in degassed acetone (10 mL) and heated gently for 30 min, whereupon a white precipitate formed. After filtering, the yellow solution was added drop-wise to a solution of Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub> (0.15 g, 0.253 mmol) in degassed toluene (15 mL). The resulting pink solution was stirred for 30 min at room temperature and reduced in volume to ca. 2 mL whereupon a pink/orange solid formed. This was then filtered off and dried in vacuo. Yield 0.18 g, 76%. Required for [C<sub>35</sub>H<sub>38</sub>BF<sub>4</sub>IrSb<sub>2</sub>]: C, 42.8; H, 3.9. Found: C, 43.6; H, 4.1%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.0–7.6 (m) [20H] (Ph), 3.76 (s) [4H] (cod CH), 2.59 (br) [8H] (cod CH<sub>2</sub>), 2.00-2.15 (m) [6H]  $(CH_2)$  ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  128.22–133.40 (Ph), 63.77 (cod CH), 36.53 (cod CH<sub>2</sub>), 23.37 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 19.59 (SbCH<sub>2</sub>) ppm. ES<sup>+</sup> MS (MeCN): m/z 895 [Ir(cod){Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub>}]<sup>+</sup>. IR (Nujol mull): 1064 ( $BF_4^{-}$ ) cm<sup>-1</sup>.

**[Ir(cod)**{*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SbMe<sub>2</sub>)<sub>2</sub>}**BF**<sub>4</sub>. Method as above using [Ir<sub>2</sub>Cl<sub>2</sub>(cod)<sub>2</sub>], AgBF<sub>4</sub> and *o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SbMe<sub>2</sub>)<sub>2</sub>. Yield 65%. Required for [C<sub>20</sub>H<sub>32</sub>BF<sub>4</sub>IrSb<sub>2</sub>]: 30.2; H, 4.1. Found: C, 30.2; H, 4.1%. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO): δ 7.2–7.7 (m) [4H] (*o*-C<sub>6</sub>H<sub>4</sub>), 3.8 (br) [8H] (cod CH, SbCH<sub>2</sub>), 2.5 (br) [8H] (cod CH<sub>2</sub>), 1.4 (s) [12H] (SbMe) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR ((CD<sub>3</sub>)<sub>2</sub>CO): δ 126.4–136.7 (*o*-C<sub>6</sub>H<sub>4</sub>), 59.16 (cod CH), 33.60 (cod CH<sub>2</sub>), 24.73 (SbCH<sub>2</sub>), -4.87 (SbMe) ppm. ES<sup>+</sup> MS (MeCN): *m/z* 707 [Ir(cod){*o*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>SbMe<sub>2</sub>)<sub>2</sub>}]<sup>+</sup>. IR (Nujol mull): 1064 (BF<sub>4</sub><sup>-</sup>) cm<sup>-1</sup>.

 $[Ir{Ph_2Sb(CH_2)_3SbPh_2}_2]BF_4.$   $[Ir_2(coe)_4Cl_2]$ (0.08)g, 0.09 mmol) and AgBF<sub>4</sub> (0.043 g, 0.22 mmol) were dissolved in degassed acetone (10 mL) and stirred at RT for 1 h. The white precipitate was filtered off and the orange solution was added dropwise to a solution of Ph<sub>2</sub>Sb(CH<sub>2</sub>)<sub>3</sub>SbPh<sub>2</sub> (0.225 g, 0.38 mmol) in degassed toluene (10 mL). The reaction was stirred for 30 min and then the reaction was pumped to dryness. The yellow residues were dissolved in minimum acetone, and Et<sub>2</sub>O (10 mL) was added to precipitate a solid. The yellow solid was isolated by filtration and dried in vacuo. Yield 0.19 g, 72%. Required for [C54H52BF4IrSb4]·CH2Cl2: C, 42.5; H, 3.5. Found: C, 41.9; H, 3.7%. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO): δ 7.0–7.4 (m) [40H] (Ph), 5.43 (s)  $CH_2Cl_2$ , 2.8 (br) [4H] (CH<sub>2</sub>), 2.3 (br) [8H] (CH<sub>2</sub>).  ${}^{13}C{}^{1}H$ NMR ((CD<sub>3</sub>)<sub>2</sub>CO): δ 130.0–136.6 (Ph), 25.0 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 23.1 (SbCH<sub>2</sub>). IR (Nujol mull): 1067 (BF<sub>4</sub><sup>-</sup>) cm<sup>-1</sup>.

#### X-Ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 2. Crystals of  $[Rh(CO){Ph_2Sb-(CH_2)_3SbPh_2}_2]PF_6\cdot3/4CH_2Cl_2$  and  $[RhCl_2{Ph_2Sb(CH_2)_3SbPh_2}-{PhClSb(CH_2)_3SbClPh}]Cl·CHCl_3$  were obtained by diffusion of hexane into a CH\_2Cl\_2 solution of the compound, or slow evaporation of CHCl\_3 from a solution of the compound in the glove box, respectively. Data collection used a Nonius Kappa CCD diffractometer (T = 120 K) and with graphite-monochromated Mo-K $\alpha$  X-radiation ( $\lambda = 0.71073$  Å). Structure solution and

Complex	$[Rh(CO)\{Ph_{2}Sb(CH_{2})_{3}SbPh_{2}\}_{2}]PF_{6}\cdot 3/4CH_{2}Cl_{2}$	$[RhCl_{2}{Ph_{2}Sb(CH_{2})_{3}SbPh_{2}}{PhClSb(CH_{2})_{3}SbClPh}]Cl\cdot CHClSh(CH_{2})_{3}SbClPh}]Cl\cdot CHClSh(CH_{2})_{3}SbClPh}]Cl- CHCLSh(CH_{2})_{3}SbClPh$
Formula	$C_{55,75}H_{53,5}Cl_{1,5}F_6OPRhSb_4$	$C_{43}H_{43}Cl_8RhSb_4$
M	1527.54	1433.28
Crystal system	Triclinic	Monoclinic
Space group	P1 (no. 2)	$P2_1/c$ (no.14)
a/Å	13.5141(10)	28.147(6)
b/Å	20.129(3)	10.9609(16)
c/Å	21.133(3)	15.724(3)
$a/^{\circ}$	74.016(5)	90
β/°	80.152(7)	104.095(8)
y/°	82.929(7)	90
$U/Å^3$	5427.5(10)	4705.2(15)
Z	4	4
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	2.426	3.096
$R_{ m int}$	0.065	0.089
Total no. reflections	94727	31249
Unique reflections	24949	9970
No. of parameters	1265	505
$R1^a \left[ I_o > 2\sigma(I_o) \right]$	0.0509	0.1057
R1ª [all data]	0.0824	0.1508
$wR_2^{b} \left[ I_o > 2\sigma(I_o) \right]$	0.0996	0.1492
$wR_2^b$ [all data]	0.1109	0.1730

# Table 2 Crystallographic parameters

<sup>*a*</sup>  $R1 = \sum ||F_o - |F_c||_i / \sum |F_o| \cdot {}^{b} w R_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w F_{oi}^4]^{1/2}.$ 

refinement were routine.<sup>34,35</sup> Selected bond lengths and angles are presented in Table 1 and the Fig. 2 caption.

CCDC reference numbers 604224 and 604225.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605198g

# Acknowledgements

We thank the EPSRC for support and access to the EPSRC's Chemical Database Service at Daresbury. We also thank Johnson-Matthey plc for loans of precious metal salts.

# References

- W. Levason and N. R. Champness, *Coord. Chem. Rev.*, 1994, **133**, 115;
   W. Levason and G. Reid, *Coord. Chem. Rev.*, 10.1016/j.ccr.2006.03. 024.
- 2 W. Levason and G. Reid, in *Comprehensive Coordination Chemistry II*, ed., J. A. McCleverty and T. J. Meyer, Elsevier, Amsterdam, 2004, vol. 1, p. 377.
- 3 H. Werner, Angew. Chem., Int. Ed., 2004, 43, 938.
- 4 H. Werner, D. A. Ortmann and O. Gevert, Chem. Ber., 1996, 129, 411; H. Werner, C. Grünwald, P. Steinert, O. Gevert and J. Wolf, J. Organomet. Chem., 1998, 565, 231; M. Mattias, J. Wolf, M. Laubender, M. Teichert, D. Stalke and H. Werner, Chem.-Eur. J., 1997, 3, 1442; E. Bleuel, O. Gevert, M. Laubender and H. Werner, Organometallics, 2000, 19, 3109; D. A. Ortmann, B. Weberndörfer, J. Schöneboom and H. Werner, Organometallics, 1999, 18, 952; D. A. Ortmann, B. Weberndörfer, K. Ilg, M. Laubender and H. Werner, Organometallics, 2002, 21, 2369; H. Werner, P. Schwab, A. Heinemann and P. Steinert, J. Organomet. Chem., 1995, 496, 207; D. A. Ortmann, O. Gevert, M. Laubender and H. Werner, Organometallics, 2001, 21, 2369; H. Werner, Organometallics, 2001, 20, 1776.
- 5 M. Jimenez-Tenorio, M. C. Puerta, I. Salcedo, P. Valerga, S. I. Costa, P. T. Gomes and K. Mereiter, *Chem. Commun.*, 2003, 1168.
- 6 J. A. Casares, P. Espinet, J. M. Martin-Alvarez, J. M. Martinez-Ilarduya and G. Salas, *Eur. J. Inorg. Chem.*, 2005, 3825.
- 7 W. Levason, M. L. Matthews, G. Reid and M. Webster, *Dalton Trans.*, 2004, 51.

- 8 W. Levason, M. L. Matthews, G. Reid and M. Webster, *Dalton Trans.*, 2004, 554.
- 9 M. D. Brown, W. Levason, G. Reid and M. Webster, *Dalton Trans.*, 2006, 1667.
- 10 L. M. Vallarino, J. Chem. Soc., 1957, 2287.
- 11 S. Otto and A. Roodt, Inorg. Chim. Acta, 2002, 331, 199.
- 12 S. Otto and A. Roodt, Acta Crystallogr., Sect. C, 2002, 58, m565.
- 13 A. Kayan, J. C. Gallucci and A. Wojcicki, *Inorg. Chem. Commun.*, 1998, 1, 446.
- 14 A. Kayan, J. C. Gallucci and A. Wojcicki, J. Organomet. Chem., 2001, 630, 44.
- 15 A. Kayan and A. Wojcicki, Inorg. Chim. Acta, 2001, 319, 187.
- 16 K. Vrieze, H. C. Volger and A. P. Praat, J. Organomet. Chem., 1968, 14, 185.
- 17 P. E. Garrou and G. E. Hartwell, J. Organomet. Chem., 1974, 69, 445.
- 18 T. Even, A. R. J. Genge, A. M. Hill, N. J. Holmes, W. Levason and M. Webster, J. Chem. Soc., Dalton Trans., 2000, 655.
- 19 L. H. Pignolet, D. H. Doughty, S. C. Nowicki and A. L. Casalnuovo, *Inorg. Chem.*, 1980, 19, 2172.
- 20 L. H. Pignolet, D. H. Doughty, S. C. Nowicki, M. P. Anderson and A. L. Casalnuovo, *J. Organomet. Chem.*, 1980, **202**, 211.
- 21 B. R. James and D. Mahajan, Can. J. Chem., 1980, 58, 996.
- 22 L. M. Vallarino, Inorg. Chem., 1965, 4, 161.
- 23 A. M. Hill, W. Levason and M. Webster, *Inorg. Chim. Acta*, 1998, 271, 203.
- 24 P. Albano and M. Aresta, J. Organomet. Chem., 1980, 190, 243.
- 25 W. Hieber and V. Frey, Chem. Ber., 1966, 99, 2614.
- 26 J. T. Mague and G. Wilkinson, J. Chem. Soc. A, 1966, 1736.
- 27 A. R. J. Genge, N. J. Hill, W. Levason and G. Reid, J. Chem. Soc., Dalton Trans., 2001, 1007.
- 28 J. A. McCleverty and G. Wilkinson, Inorg. Synth., 1966, 8, 211.
- 29 G. Giordano and R. H. Crabtree, Inorg. Synth., 1979, 19, 218.
- 30 J. L. Herde, J. C. Lambert and C. V. Senoff, Inorg. Synth., 1974, 15, 18.
- 31 A. van der Ent and A. L. Onderdelinden, Inorg. Synth., 1990, 28,
- 90.
  32 S. Sato, Y. Matsumura and R. Okawara, J. Organomet. Chem., 1972, 43, 333.
- 33 H. A. Meinema, H. F. Martens and J. G. Noltes, J. Organomet. Chem., 1976, 110, 183.
- 34 G. M. Sheldrick, SHELXS-97, program for crystal structure solution, University of Göttingen, Germany, 1997.
- 35 G. M. Sheldrick, SHELXL-97, program for crystal structure refinement, University of Göttingen, Germany, 1997.