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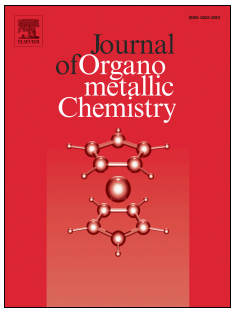

Rhodium(III) and Iridium(III) Half-Sandwich Complexes with Tertiary Arsine and Stibine Ligands

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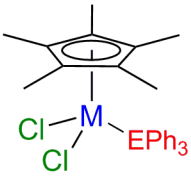


M = Rh, Ir
E = As, Sb

E	Rh-E (Å)	ΔG_{calc} (kJ mol^{-1})
P	2.318	-75.0
As	2.430	-51.0
Sb	2.575	-53.5

Rhodium(III) and Iridium(III) Half-Sandwich Complexes with Tertiary Arsine and Stibine Ligands

Brian A. Chalmers, Michael Bühl, Phillip S. Nejman, Alexandra M. Z. Slawin, J. Derek Woollins and Petr Kilian*

EaStChem School of Chemistry, University of St Andrews, St Andrews, Fife, KY16 9ST, UK.

*Corresponding author: email pk7@st-andrews.ac.uk, phone +44 1334 467304, fax +44 1334 463808

Keywords: Arsine; Stibine; Rhodium; Iridium; Half-Sandwich complex; DFT Calculations

Abstract

The syntheses of rhodium(III) and iridium(III) half sandwich complexes containing tertiary arsine and stibine ligands of the form $[Cp^*M(L)Cl_2]$ (M = Rh, Ir; L = $AsEt_3$, $AsPh_3$, $SbPh_3$) are reported. These compounds represent infrequent examples of rhodium and iridium metal complexes bearing arsenic or antimony ligands. All new compounds were fully characterised using ^1H and ^{13}C NMR spectroscopy, mass spectrometry and single crystal X-ray diffraction. DFT calculations show the formation of the complexes from $(Cp^*MCl_2)_2$ and EPh_3 (E = P, As, Sb) to be highly exothermic, although the enthalpic driving force is decreasing in the expected sequence P > As > Sb.

Introduction

The dinuclear rhodium and iridium complexes $[Cp^*RhCl_2]_2$ and $[Cp^*IrCl_2]_2$ are easily prepared by reacting $RhCl_3$ or $IrCl_3$ hydrates with pentamethylcyclopentadiene (Cp^*H) as first reported by Maitlis.[1] The dimers are split to mononuclear complexes upon quantitative reactions with triethylphosphine, resulting in $[Cp^*Rh(PEt_3)Cl_2]$ and $[Cp^*Ir(PEt_3)Cl_2]$ as air stable solids.[2] The crystal structures of these two compounds were recently determined within our research group.[3] In these triethylphosphine complexes the chloride ligands can be displaced by a range of other ligands such as selenide, telluride, azide and acetate, which makes them rather versatile synthons.[3-4] In sharp contrast to phosphines, a search of the Cambridge Structural Database (CSD) for Cp^*RhCl_2 and Cp^*IrCl_2 fragments coordinated to arsine or stibine ligands resulted in zero hits.

A few rhodium complexes with arsine and stibine ligands are known such as the Rh(I) chelate complex $[(Ph_2AsCH_2AsPh_2)Rh(CO)Cl]_2$ **(A)**,[5] *trans*-$[(Ph_3Sb)_2Rh(CO)Cl]$ **(B)**[6] and a Rh(III) complex *mer*–$[(Ph_3Sb)_3RhCl_3]$ **(C)**[7] (Figure 1). Iridium containing complexes with arsenic and antimony ligands are much rarer with only a few known, including *trans*-$[IrHCl(\eta^3\text{-}C_3H_5)(Sb\textit{i}Pr_3)_2]$ **(D)** and *trans*-$[IrHCl(\eta^3\text{-}C_8H_{13})(Sb\textit{i}Pr_3)_2]$ **(E)**[8]. Kemmitt reacted $RhCl_3{\cdot}xH_2O$, $RhCl_2(C_2H_4)_4$ and $Rh_2(CO)_4Cl_2$ precursors with a series of rather electron poor pnictine ligands $(C_6F_5)_3E$, $(C_6F_5)_2PhE$ and $(C_6F_5)Ph_2E$ (E = P, As, Sb).[9] While all the phosphines formed expected complexes, of arsine ligands only $(C_6F_5)Ph_2As$ and $Rh_2(CO)_4Cl_2$ gave the expected complex $[(C_6F_5)Ph_2As]_2Rh(CO)Cl$ **(F)**, while no reaction was observed for all other arsine ligands. No reaction took place between any of the stibine ligands and rhodium precursor complexes. Kemmitt also used K_2PtCl_4 and PtX_2 (X = Cl, Br, I) as reactants in this study. These gave similar results with no stibine complexes being formed, although $(C_6F_5)Ph_2As$ did form the expected Pt complexes.[9] The arsine and stibine complexes *cis*-$[PtCl_2(AsEt_3)]$ and *cis*-$[PtCl_2(AsMe_2Ph)_2]$ are also known although it is still evident that phosphine complexes of transition metals are far more prevalent than As and Sb complexes.[10][11]

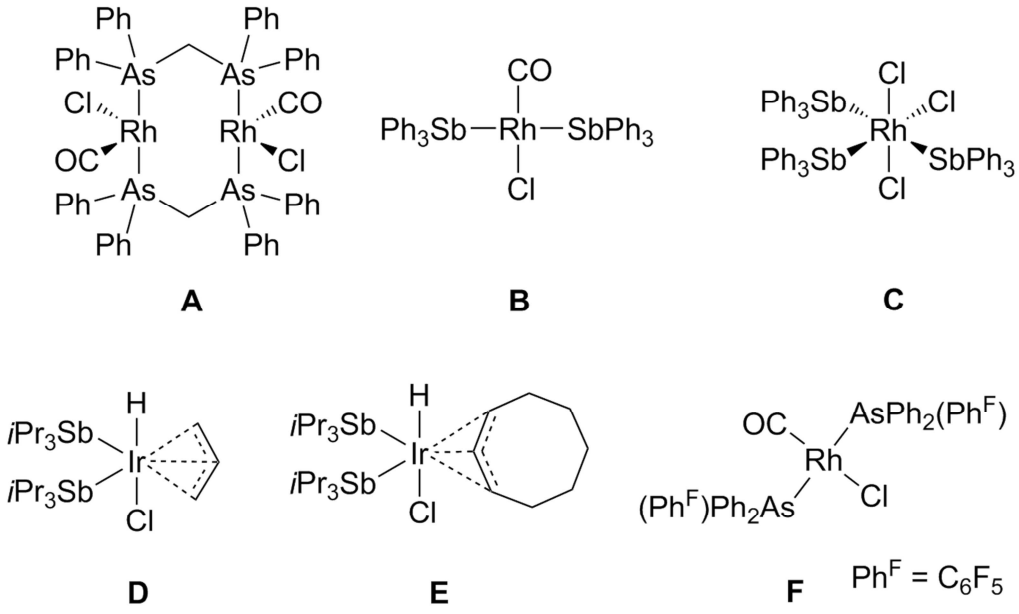


Figure 1: Examples of rhodium and iridium complexes with arsine and stibine ligands.

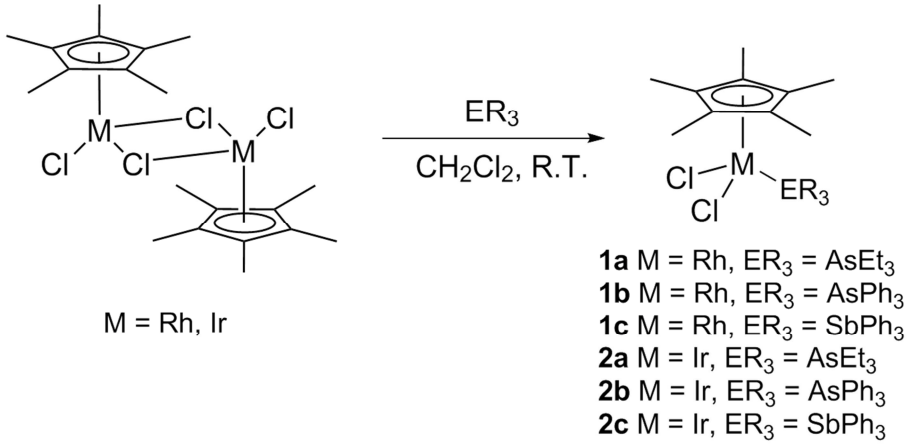
In this paper we report the synthesis of six novel mononuclear complexes, **1a**–**c** and **2a**–**c**, of the form $[Cp^*M(ER_3)Cl_2]$ (M = Rh, Ir; E = As, Sb, R = Et, Ph). These complexes are potential synthons as the chloride ligands are likely to be easily displaced by a range of other ligands (as discussed for the related triethylphosphine complexes above). The complexes are easily prepared in excellent yields and good purity and are thermally stable (m.p. >190°C), in particular no signs of pnictine

ligands elimination were observed at room or elevated temperatures. In addition, the complexes are fully air and moisture stable.

Results & Discussion

Synthesis and NMR

The addition of two molar equivalents of triethylarsine to a dichloromethane solution of $[Cp^*MCl_2]_2$ (M = Rh, Ir) at room temperature and subsequent removal of the volatiles after two hours of stirring resulted in the desired mononuclear complexes **1a** $[Cp^*Rh(AsEt_3)Cl_2]$ and **2a** $[Cp^*Ir(AsEt_3)Cl_2]$ in near quantitative yields (>98%) (Scheme 1).



Scheme 1: Syntheses reported in this paper.

In the ^{1}H NMR spectra of **1a** and **2a**, a noticeable shift towards higher frequency is seen for CH_2 as well as CH_3 groups of the ethyl substituents, consistent with transfer of the electron density from the arsenic atom upon coordination to the metal centre [**1a**: δ_H 2.04 (q) and 1.23 (t); **2a**: δ_H 2.05 (q) and 1.21 (t); *cf.* $AsEt_3$: δ_H 1.26 (q) and 1.06 (t), see Figure S1 in Supporting Information]. The methyl groups of the Cp* ligands in $[Cp^*M(AsEt_3)Cl_2]$ (**1a** and **2a**) also show a slight high frequency shift (*ca.* 0.1 ppm) *cf.* the precursor $[Cp^*MCl_2]_2$ complexes.

The reactions of EPh_3 (E = As, Sb) with $[Cp^*MCl_2]_2$ (M = Rh, Ir) at room temperature gave the expected mononuclear pnictine complexes **1b** $[Cp^*Rh(AsPh_3)Cl_2]$, **1c** $[Cp^*Rh(SbPh_3)Cl_2]$, **2b** $[Cp^*Ir(AsPh_3)Cl_2]$, and **2c** $[Cp^*Ir(SbPh_3)Cl_2]$ in excellent yields (93–99%) (Scheme **1**). Similarly to compounds **1a** and **2a**, the *ortho* hydrogens of the phenyl group resonances in **1b**, **1c**, **2b** and **2c** show a noticeable high frequency shift of around 0.2 ppm in the ^{1}H NMR spectra compared to those

in uncoordinated $AsPh_3$ and $SbPh_3$. The homogeneity of **1a–c** and **2a–c** was confirmed by microanalysis and high-resolution mass spectrometry.

Structural Analysis

Crystal structures of all new complexes were determined; these are shown in Figure 2 and in Table 1. Crystals for X-ray diffraction work were grown from either acetone, dichloromethane or 1,2-dichloroethane at room temperature. Compounds **1a, 1c**, **2a–2c** have two or three independent molecules in the asymmetric units all of which have very similar geometries. Values presented in the discussion of these molecules are the mean values. Data for **2a** is of somewhat lower quality, but is sufficient to demonstrate the connectivity of the molecule; the bond lengths and angles are in line with those observed in the other molecules. All of the complexes (**1a–c** and **2a–c**) are isostructural and attain piano stool geometry (around the metal centre) with the η^5–Cp* ring slightly tilted, as shown by the slight variation in the M–C bond lengths (see Table 1 and Figure 2). The M-E and M-C (M = Ir, Rh; E = As, Sb) bonds are all as expected.[14] The pnictogen ligands adopt tetrahedral geometry, again, with normal As–C and Sb–C bond lengths and angles.

Comparing the $AsPh_3$ and $SbPh_3$ complexes (**1b** *vs.* **1c** and **2b** *vs.* **2c**) the difference in Rh–E and Ir–E (E = As, Sb) bond lengths is up to 6%; this is somehow smaller than expected from the differences in covalent radii (r_{cov} As 1.19 Å; Sb 1.39 Å, 14% difference).[15] The M–Cl bonds in all compounds fall within the expected range of other half sandwich complexes.

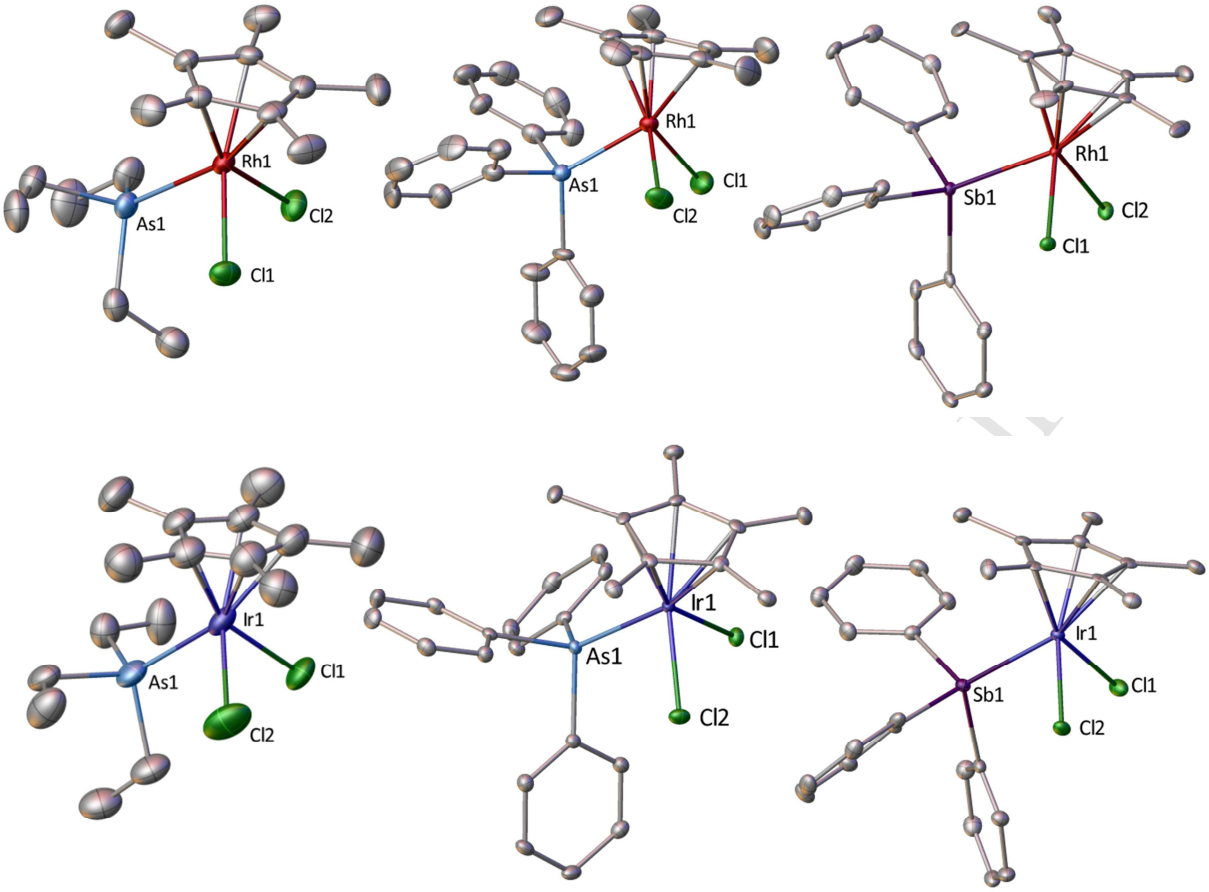


Figure 2: Ellipsoid plots of the crystal structures of **1a** (top left), **1b** (top centre), **1c** (top right), **2a** (bottom left), **2b** (bottom centre) and **2c** (bottom right) with hydrogen atoms, solvating molecules (for **1b**) and other molecules in the asymmetric unit are omitted. Ellipsoids are drawn at the 40% level.

Table 1: Selected bond lengths (Å) and angles (°) **1a**–**c** and **2a**–**c**. Compounds with multiple molecules in the asymmetric unit have their values reported as ranges.

	1a	**1b**·CH_2Cl_2	**1c**
Rh–E	2.425(1)–2.4372(9)	2.444(1)	2.5703(7)/2.5733(8)
Rh–Cl	2.394(2)–2.428(2)	2.397(3)/2.418(3)	2.397(1)–2.424(2)
Rh–C	2.13(1)–2.214(7)	2.16(1)–2.22(1)	2.145(5)–2.200(6)
Cl–Rh–Cl	92.10(6)–97.22(6)	91.2(1)	91.81(5)/90.64(5)
E–Rh–Cl	85.43(5)–88.07(6)	85.62(8)/90.35(8)	84.27(4)–86.01(4)
	2a	**2b**	**2c**
Ir–E	2.381(4)/2.384(3)	2.4269(7)/2.4333(7)	2.5742(8)/2.5761(7)
Ir–Cl	2.383(6)–2.42(1)	2.408(1)–2.413(1)	2.407(1)–2.426(1)
Ir–C	2.10(3)–2.21(4)	2.156(4)–2.211(4)	2.153(4)–2.217(4)
Cl–Ir–Cl	87.6(3)/88.6(3)	89.05(3)/90.06(3)	87.90(4)/89.04(4)
E–Ir–Cl	86.4(2)–89.2(2)	86.49(3)–87.30(3)	84.76(3)–86.16(3)

Computational Analysis

To complement the experimental findings, we performed density functional theory (DFT) calculations at an appropriate level, BP86-D3. Computed metal-pnictogen distances, Wiberg bond indices (WBIs)[16] as well as enthalpies and free energies for the formation reaction according to Eq. 1 are collected in

Table **2**.

$$½\ [Cp^*MCl_2]_2 + EPh_3 \rightarrow Cp^*M(EPh_3)Cl_2\ (M = Rh, Ir;\ E = P, As, Sb) \qquad \text{Eq. 1}$$

Table 2: Metal-pnictogen (M–E) bond distances (in Å) observed in the crystal and calculated at the BP86-D3 level (SDD/6-31G* basis). Wiberg bond indices obtained at the same level are given in square brackets. Calculated reaction enthalpies and free energies (in kJ mol^{-1}) according to Eq. 1.

Compd. (M/E)	$d_{M–E}$ (X-ray)†	$d_{M–E}$ (calc) [WBI]	*ΔH*	*ΔG*
(Rh / P) ‡	2.341	2.295 [0.68]	–116.3	–75.0
1b (Rh / As)	2.444	2.394 [0.68]	–95.3	–51.0
1c (Rh / Sb)	2.573/2.570	2.539 [0.71]	–78.0	–53.5

(Ir / P) [§]	2.318	2.296 [0.78]	–138.2	–98.4
2b (Ir / As)	2.433/2.427	2.404 [0.76]	–110.2	–66.3
2c (Ir / Sb)	2.574/2.576	2.561 [0.78]	–90.9	–59.0

†This work (except where otherwise noted); values are given for all independent molecules in the asymmetric unit (one or two). [‡] CSD ref. code AKOVEC.[17] [§] CSD ref. code VOGZOH.[18]

All reactions according to Eq. 1 are computed to be highly exothermic, with the absolute enthalpic driving forces decreasing in the expected sequence P > As > Sb for either metal (see ΔH values in Table **2**). Notably, the driving force for $SbPh_3$ coordination still accounts to 67% (Rh) and 66% (Ir) of that for PPh_3.[19] This sequence is not reflected in the M–E WBIs, which are not very sensitive toward the nature of pnictogen E, adopting values around *ca.* 0.7 and 0.8 for M = Rh and Ir, respectively. Both computed WBIs and driving forces agree that the bonds involving iridium are slightly stronger than those involving rhodium (by *ca.* 12–22 kJ/mol in terms of ΔH).

Conclusions

A series of novel Rh(III) and Ir(III) η^5–Cp* half sandwich complexes with arsine and stibine ligands have been prepared and fully characterised by ^{1}H and ^{13}C NMR spectroscopy, elemental microanalysis and high resolution mass spectrometry. All of the six novel compounds were structurally characterised and shown to display only small deviations in the M–E bond lengths and overall geometries. Complementary DFT calculations indicated the expected trend, in that the more Lewis basic pnictogens have a higher formation enthalpy, although M–E bond WBIs remain essentially constant within each metal series. Synthetic applications of here reported complexes, such as in the formation of multimetallic systems, and chloride ligand metathesis will be investigated next.

Experimental Section

General Considerations

Synthetic manipulations for compounds **1a** and **2a** were performed under an atmosphere of nitrogen using standard Schlenk-line techniques. Dry solvents were collected from an *MBraun Solvent Purification System* and stored over molecular sieves. Chemicals were purchased from Sigma Aldrich, Alfa Aesar, Precious Metals Online or were taken from the laboratory inventory and used

without further purification. The two precursor metal complexes $[Cp^*MCl_2]_2$ (M = Rh, Ir) were prepared in good yields *via* the reaction of the chlorides $MCl_3 \cdot 3H_2O$ with Cp*H.[1] Triethylarsine was prepared *via* the reaction of excess ethylmagnesium bromide with arsenic trichloride,[20] which in turn was prepared by the reaction of As_2O_3 with $SOCl_2$.[21] All NMR spectra were recorded using a Bruker Avance 500 or Bruker Avance III 500 spectrometer at 25 °C. ^{13}C NMR spectra were recorded using the DEPT-Q–135 pulse sequence with broadband proton decoupling. In ^{1}H and ^{13}C NMR, tetramethylsilane was used as a reference. Residual solvent peaks were also used for calibration (CD_2Cl_2 δ_H 5.36, δ_C 53.5 ppm). Chemical shifts (δ) are given in parts per million (ppm) and coupling constants (*J*) are given in Hertz (Hz). Infrared spectra were recorded as KBr discs (range 4000–200 cm^{-1}); Raman spectra were recorded on solid samples in glass capillaries using a dipole pumped NdYAG excitation laser (range 3500–150 cm^{-1}), both using a Perkin-Elmer System 2000 NIR/Raman FT Spectrometer. Melting points were determined in sealed glass capillaries using a Stuart SMP 30 melting point apparatus. Mass Spectrometry was carried out at either the University of St Andrews Mass Spectrometry Service by Mrs Caroline Horsburgh or at the EPSRC UK National Mass Spectrometry Facility in Swansea. Elemental microanalysis was performed by Mr Stephen Boyer at London Metropolitan University.

DFT Calculations

Geometries were fully optimized at the BP86-D3/6-31G* level; [22][23] Rh, Ir and Sb were described with relativistically adjusted effective core potentials from the Stuttgart-Dresden groups (denoted SDD) with the associated valence basis sets[24] (the Sb basis was augmented with a set of d-polarization functions), As was described with the 962(d) all-electron Binning-Curtiss basis. See Supporting Information for further details and references.

Synthetic Methods

$[Cp^*Rh(AsEt_3)Cl_2]$ (1a): Under an atmosphere of dry nitrogen, a solution of $[Cp^*RhCl_2]_2$ (300 mg, 485 µmol) in dichloromethane (10 mL) was prepared. To this a solution of $AsEt_3$ (160 mg, 0.14 mL, 970 µmol) in dichloromethane (10 mL) was added in one portion. After stirring for two hours at ambient temperature, the volatiles were removed *in vacuo* to give an air-stable red powder (452 mg, 99%) (Mp. 200 °C). Crystals suitable for X-ray diffraction were grown from acetone at ambient temperature. **Elemental Analysis:** Calcd. (%) for $C_{16}H_{30}Cl_2AsRh$ (471.14 $gmol^{-1}$): C 40.79, H 6.41. Found: C 40.75, H 6.42. **^{1}H NMR:** δ_H (500.1 MHz, CD_2Cl_2) 2.04 (6H, q, $^{3}J_{HH}$ = 7.8 Hz, CH_2), 1.69 (15H, s, CH_3, Cp*), 1.23 (9H, t, $^{3}J_{HH}$ = 7.8 Hz, CH_3). **$^{13}C\{^{1}H\}$ NMR:** δ_C (125.8 MHz, CD_2Cl_2) 96.5 (d, $^{1}J_{CRh}$ = 7.3 Hz, qC), 14.6 (s, CH_2), 9.2 (s, 5×CH_3, Cp*), 9.0 (s, CH_3). **Infrared:** (KBr disc, cm^{-1}) ν = 2958s (ν_{C-H}), 2871s,

1450s, 1374s, 1027vs, 744s, 582s. **Raman:** (glass capillary, cm^{-1}) ν = 2959m, 2920s (ν_{Ar-H}), 617s, 589s, 551s, 413vs, 282s. **HRMS (ES+):** *m/z* (%) Calcd. for $C_{16}H_{30}ClAsRh$: 435.0307, found 435.0298 [M–Cl].

[Cp*Rh(AsPh$_3$)Cl$_2$] (1b): Solid $[Cp^*RhCl_2]_2$ (295 mg, 477 µmol) was added to a flask containing solid $AsPh_3$ (300 mg, 978 µmol). Dichloromethane (20 mL) was added, and the solution was left to stir for 2 hours at ambient temperature. The volatiles were removed *in vacuo* to give a red powder (534 mg, 93%) (Mp. 251 °C with decomposition). Crystals suitable for X-ray diffraction were grown from dichloromethane at room temperature. **Elemental Analysis:** Calcd. (%) for $C_{28}H_{30}Cl_2AsRh$ (615.27 $gmol^{-1}$): C 54.66, H 4.91. Found: C 54.76, H 4.86. **^{1}H NMR:** δ_H (500.1 MHz, CD_2Cl_2) 7.81–7.75 (6H, m, o–Ph), 7.50–7.37 (9H, m, *m*–Ph, *p*–Ph), 1.45 (15H, s, 5×CH_3, Cp*). **^{13}C{^{1}H} NMR:** δ_C (125.8 MHz, CD_2Cl_2) 134.1 (s, *o*–Ph), 133.8 (s, C_{ipso}), 130.0 (s, *p*–Ph), 128.5 (s, *m*–Ph), 97.5 (s, C_{ipso}, Cp*), 8.7 (s, CH_3, Cp*). **Infrared:** (KBr disc, cm^{-1}) ν = 3049m ($\nu_{Ar–H}$), 2959m ($\nu_{C–H}$), 1489s, 1437s, 1078s, 1025s, 740vs, 659vs, 477s. **Raman:** (glass capillary, cm^{-1}) ν = 3055s, 2914s, 1003vs, 415s. **HRMS (ES+):** *m/z*: Calcd. (%) for $C_{28}H_{30}AsClRh$: 579.0307, found 579.0290 (100) [M–Cl]; Calcd. for $C_{12}H_{18}NClRh$: 314.0183 (95) [M–Cl–$AsPh_3$ + MeCN], found 314.0170; Calcd. for $C_{10}H_{15}ClRh$: 272.9917, found 272.9906 (25) [M–Cl–$AsPh_3$].

[Cp*Rh(SbPh$_3$)Cl$_2$] (1c): This was prepared as per compound **1b** using $[Cp^*RhCl_2]_2$ (150 mg, 242 µmol) and $SbPh_3$ (171 mg, 485 µmol) giving **1c** as a red solid (317 mg, 99%) (Mp. 235 °C with decomposition). Crystals suitable from X-ray diffraction were grown from slow diffusion of hexane into a saturated solution of **1c** in dichloromethane. **Elemental Analysis:** Calcd. (%) for $C_{28}H_{30}Cl_2SbRh$ (662.11 $gmol^{-1}$): C 50.79, H 4.57. Found: C 50.66, H 4.59. **^{1}H NMR:** δ_H (500.1 MHz, CD_2Cl_2) 7.78–7.75 (6H, m, *o*–Ph), 7.49–7.42 (9H, m, *m*–Ph, *p*–Ph), 1.61 (15H, s, 5×CH_3, Cp*). **^{13}C{^{1}H} NMR:** δ_C (125.8 MHz, CD_2Cl_2) 136.2 (s, *o*–Ph), 131.2 (s, C_{ipso}), 130.2 (s, *p*–Ph), 129.0 (s, *m*–Ph), 97.1 (d $^1J_{CRh}$ = 7.6 Hz, C_{ipso}, Cp*), 9.1 (s, 5 × CH_3). **Infrared:** (KBr disc, cm^{-1}) ν = 3047m ($\nu_{Ar–H}$), 2957m ($\nu_{C–H}$), 1432s, 1022s, 743s, 733vs, 694s, 453s. **Raman**: (glass capillary, cm^{-1}) ν = 3056s ($\nu_{Ar–H}$), 2915s ($\nu_{C–H}$), 1001vs, 658s, 421s. **HRMS (ES+):** *m/z* (%) Calcd. for $C_{28}H_{30}ClSbRh$: 625.0129, found 625.0105 (100) [M–Cl].

[Cp*Ir(AsEt$_3$)Cl$_2$] (2a): This was prepared as per compound **1a** using $[Cp^*IrCl_2]_2$ (200 mg, 250 µmol) and $AsEt_3$ (81 mg, 170 µL, 500 µmol) giving **2a** as an orange solid (275 mg, 98%) (Mp. 194 °C). Crystals suitable for X-ray diffraction were grown from acetone at ambient temperature. **Elemental Analysis:** Calcd. (%) for $C_{16}H_{30}Cl_2AsIr$ (560.45 g mol^{-1}): C 34.29, H 5.39. Found: C 34.18, H 5.38. **^{1}H NMR:** δ_H (500.1 MHz, CD_2Cl_2) 2.05 (6H, q, $^3J_{HH}$ = 7.8 Hz, CH_2), 1.70 (15H, s, 5×CH_3, Cp*), 1.21 (9H, t, $^3J_{HH}$ = 7.8 Hz, CH_3) **^{13}C{^{1}H} NMR:** δ_C (125.8 MHz, CD_2Cl_2) 89.1 (s, C_{ipso}, Cp*), 13.4 (s, CH_2), 8.9 (s, CH_3, Cp*), 8.6 (s, CH_3). **Infrared:** (KBr disc, cm^{-1}) ν = 2930s ($\nu_{C–H}$), 1452s, 1376s, 1031vs, 733s. **Raman:**

(glass capillary, cm^{-1}) ν = 2918s (ν_{Ar-H}), 591s, 561s, 412s, 288s. **HRMS (ACPI+):** *m/z* (%) Calcd. for $C_{26}H_{45}Cl_3AsIr_2$: 923.1062, found 923.1029 (10) [2M–Cl–$AsEt_3$]; Calcd. for $C_{16}H_{31}Cl_2AsIr$: 560.0648, found 561.0631 (20) [M+H]; Calcd. for $C_{16}H_{30}ClAsIr$: 525.0868, found 525.0862 (70) [M–Cl]; Calcd. for $C_6H_{16}As$: 163.0468, found 163.0459 (100) [Et_3As+H].

[Cp*Ir(AsPh$_3$)Cl$_2$] (2b): This was prepared as per compound **1b** using $[Cp^*IrCl_2]_2$ (200 mg, 250 µmol) and $AsPh_3$ (154 mg, 500 µmol) giving **2b** as an orange solid (351 mg, 99%) (Mp. 283 °C). Crystals suitable for X-ray diffraction were grown from 1,2-dichloroethane at ambient temperature. **Elemental Analysis:** Calcd. (%) for $C_{28}H_{30}Cl_2AsIr$ (704.58 $gmol^{-1}$): C 47.73, H 4.29. Found: C 47.83, H 4.20. **^{1}H NMR:** δ_H (500.1 MHz, CD_2Cl_2) 7.77–7.74 (6H, m, *o*–Ph), 7.48–7.41 (9H, m, *m*–Ph, *p*–Ph), 1.45 (15H, s, 5×CH_3, Cp*). **^{13}C{^{1}H} NMR:** δ_C (125.8 MHz, CD_2Cl_2) 134.1 (s, *o*–Ph), 133.2 (s, C_{ipso}), 130.1 (s, *p*–Ph), 128.4 (s, *m*–Ph), 90.3 (s, C_{ipso}, Cp*), 8.3 (s, CH_3). **Infrared:** (KBr disc, cm^{-1}) ν = 3054m ($\nu_{Ar–H}$), 2987m ($\nu_{C–H}$), 1484s, 1436vs, 1078s, 1027s, 741vs, 695vs, 483s. **Raman:** (glass capillary, cm^{-1}) ν = 3056s, 2918m (ν_{Ar-H}), 1582s, 1003vs, 416s, 291s. **HRMS (APCI+):** *m/z* (%) Calcd. for $C_{28}H_{30}Cl_2AsIr$: 704.0551, found 704.0551 (45) [M^+]; Calcd. for $C_{28}H_{30}ClAsIr$: 669.0881, found 669.0860 (20) [M–Cl]; Calcd. for $C_{18}H_{16}As$: 307.0468, found 307.0459 (100) [Ph_3As+H].

[Cp*Ir(SbPh$_3$)Cl$_2$] (2c): This was prepared as per compound **1b** using $[Cp^*IrCl_2]_2$ (150 mg, 188 µmol) and $SbPh_3$ (133 mg, 376 µmol) giving **2c** as an orange solid (280 mg, 99%) (Mp. 213 °C). Crystals suitable for X-ray diffraction were grown from dichloromethane at ambient temperature. **Elemental Analysis:** Calcd. (%) for $C_{28}H_{30}Cl_2SbIr$ (751.42 $gmol^{-1}$): C 44.76, H 4.02. Found: C 44.64, H 4.02. **^{1}H NMR:** δ_H (500.1 MHz, CD_2Cl_2) 7.77–7.74 (6H, m, *o*–Ph), 7.51–7.42 (9H, m, *o*–Ph, *p*–Ph), 1.61 (15H, s, 5×CH_3, Cp*). **^{13}C{^{1}H} NMR:** δ_C (125.8 MHz, CD_2Cl_2) 136.2 (s, *o*–Ph), 130.2 (s, *p*–Ph), 129.8 (s, C_{ipso}), 129.0 (s, *m*–Ph), 89.9 (s, C_{ipso}, Cp*), 8.7 (s, CH_3). **Infrared:** (KBr disc, cm^{-1}) ν = 3048m ($\nu_{Ar–H}$), 2960m ($\nu_{C–H}$), 1432s, 733vs, 694vs, 462s. **Raman**: (glass capillary, cm^{-1}) ν = 3048s ($\nu_{Ar–H}$), 2920s ($\nu_{C–H}$), 1001vs, 659s, 419s. **HRMS (ES+):** *m/z* (%) Calcd. for $C_{28}H_{20}ClSbIr$: 715.0704, found 715.0669 (100) [M–Cl].

X-ray Diffraction and Computational Details

The crystallographic and computational details relating to this work can be found in the supporting information available as a free download. CCDC 1410325-1410330 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data_request/cif.

Notes

The author declares no competing financial interest.

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Highlights

- Synthesis of novel, air-stable tertiary arsine and stibine complexes of Rh(III) and Ir(III)
- Full spectral and crystallographic characterisation of novel half-sandwich complexes
- Crystallographic studies of Group 9 metal complexes with heavier Group 15 ligands
- DFT calculations of enthalpies and free energies for the formation reaction

References

1. C. White, A. Yates, P. M. Maitlis, *Inorg. Synth.* 1992, **29**, 228-234.
2. (a) J. W. Kang, K. Moseley, P. M. Maitlis, *J. Am. Chem. Soc.* 1969, **91**, 5970-5977; (b) I. Ara, J. R. Berenguer, E. Eguizábal, J. Forniés, E. Lalinde, A. Martín, F. Martínez, *Organometallics* 1998, **17**, 4578-4596.
3. P. S. Nejman, B. Morton-Fernandez, N. Black, D. B. Cordes, A. M. Z. Slawin, P. Kilian, J. D. Woollins, *J. Organomet. Chem.* 2015, **776**, 7-16.
4. (a) P. Portius, A. J. H. M. Meijer, M. Towrie, B. F. Crozier, I. Schiager, *Dalton Trans.* 2014, **43**, 17694-17702; (b) D. A. Freedman, K. R. Mann, *Inorg. Chem.* 1991, **30**, 836-840; (c) M. Herberhold, T. Daniel, D. Daschner, W. Milius, B. Wrackmeyer, *J. Organomet. Chem.* 1999, **585**, 234-240; (d) L. Andreucci, P. Diversi, G. Ingrosso, A. Lucherini, F. Marchetti, V. Adovasio, M. Nardelli, *J. Chem. Soc., Dalton Trans.* 1986, 477-487; (e) R. Bertani, P. Diversi, G. Ingrosso, A. Lucherini, F. Marchetti, V. Adovasio, M. Nardelli, S. Pucci, *J. Chem. Soc., Dalton Trans.* 1988, 2983-2994; (f) W. Rigby, P. M. Bailey, J. A. McCleverty, P. M. Maitlis, *J. Chem. Soc., Dalton Trans.* 1979, 371-381; (g) M. Herberhold, G.-X. Jin, A. L. Rheingold, *Z. Anorg. Allg. Chem.* 2005, **631**, 135-140.
5. (a) M. Cowie, S. K. Dwight, *Inorg. Chem.* 1981, **20**, 1534-1538; (b) J. T. Mague, *Inorg. Chem.* 1969, **8**, 1975-1981.
6. S. Otto, A. Roodt, *Inorg. Chim. Acta* 2002, **331**, 199-207.
7. R. Cini, G. Tamasi, S. Defazio, M. Corsini, F. Berrettini, A. Cavaglioni, *Polyhedron* 2006, **25**, 834-842.
8. D. A. Ortmann, O. Gevert, M. Laubender, H. Werner, *Organometallics* 2001, **20**, 1776-1782.
9. R. D. W. Kemmitt, D. I. Nichols, R. D. Peacock, *J. Chem. Soc. A* 1968, 2149-2152.
10. As an example, a search of the CSD for Rh–E fragments (E = P, As, Sb) returned 43 hits for E = Sb, 67 hits for E = As and 5,450 hits for E = P.
11. (a) S. Otto, A. J. Muller, *Acta Crystallogr. Sect. C-Cryst. Struct. Commun.* 2001, **57**, 1405-1407; (b) S. Otto, M. H. Johansson, *Inorg. Chim. Acta* 2002, **329**, 135-140; (c) P. P. Phadnis, V. K. Jain, A. Klein, M. Weber, W. Kaim, *Inorg. Chim. Acta* 2003, **346**, 119-128; (d) O. F. Wendt, A. Scodinu, L. I. Elding, *Inorg. Chim. Acta* 1998, **277**, 237-241.
12. H. Werner, W. Paul, R. Zolk, *Angew. Chem. Int. Ed. Engl.* 1984, **23**, 626-627.
13. H. Köpf, U. Görges, *Z. Naturforsch., B: Chem. Sci.* 1981, **36b**, 1205-1207.

14. A search of the CSD for Rh–As bonds gave a mean value of 2.443 Å (67 hits); Ir–As bonds gave a mean value of 2.44 Å (29 hits); Rh–Sb bonds gave a mean value of 2.59 Å (43 hits) and Ir–Sb bonds gave a mean of 2.61 Å (8 hits).
15. B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reves, J. Echeverria, E. Cremades, F. Barragan, S. Alvarez, *Dalton Trans.* 2008, 2832-2838.
16. The WBI is a measure for the covalent character of a bond and adopts values close to 1 for true single bonds: Wiberg, K. B. Tetrahedron, 1968, 24, 1083-1096.
17. B. A. Paz-Michel, F. J. González-Bravo, L. S. Hernández-Muñoz, M. A. Paz-Sandoval, *Organometallics* 2010, **29**, 3709-3721.
18. B. Paz-Michel, M. Cervantes-Vazquez, M. A. Paz-Sandoval, *Inorg. Chim. Acta* 2008, **361**, 3094-3102.
19. Driving forces are slightly smaller for $AsEt_3$ than for $AsPh_3$, cf. results for **1a** in the Supporting Information.
20. W. A. Herrmann, H. H. Karsch, *Synthetic Methods of Organometallic and Inorganic Chemistry Vol 3: Phosphorus, Arsenic, Antimony and Bismuth, Vol. 3*, Thieme, New York, **1996**.
21. K. S. Pandey, A. Steiner, W. H. Roesky, S. Kamepalli, A. H. Cowley, *Inorg. Synth.* 1997, **31**, 148-150.
22. Empirical three-body dispersion correction from: S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104.
23. (a) A. D. Becke, *Phys. Rev. A* 1988, **38**, 3098-3100; (b) J. P. Perdew, *Phys. Rev. B* 1986, **33**, 8822-8824; (c) J. P. Perdew, *Phys. Rev. B* 1986, **34**, 7406-7406.
24. (a) P. Schwerdtfeger, M. Dolg, W. H. E. Schwarz, G. A. Bowmaker, P. D. W. Boyd, *J. Chem. Phys.* 1989, **91**, 1762-1774; (b) A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, *Mol. Phys.* 1993, **80**, 1431-1441.

Supporting Information for

Rhodium(III) and Iridium(III) Half-Sandwich Complexes with Tertiary Arsine and Stibine Ligands

Brian A. Chalmers, Michael Bühl, Phillip S. Nejman, Alexandra M. Z. Slawin, J. Derek Woollins and Petr Kilian*

EaStChem School of Chemistry, University of St Andrews, St Andrews, Fife, KY16 9ST, UK.

*Corresponding author email: pk7@st-andrews.ac.uk

Preparation of $AsCl_3$ and Et_3As

The procedures for $AsCl_3$ and Et_3As have been adapted slightly from literature sources and additional observations made. All experiments should be performed with the cited original reports in hand. Instrumentation and general experimental conditions are provided in the main manuscript.

Arsenic(III) Chloride [1]

In a 500 mL three-necked round bottom flask (equipped with water condenser, dropping funnel and young's adapters) arsenic(III) oxide (100.0 g, 0.51 mol) was added. To this thionyl chloride (327.0 g, 200 mL, 2.75 mol) was added to the dropping funnel. The thionyl chloride was added cautiously in 50 mL portions to the As_2O_3 every ½ hour. Sulfur dioxide was furiously evolved during the first addition causing the solution to boil vigorously. Once all the thionyl chloride had been added, the yellow solution was left to stir for a further 40 hours at room temperature. The flask was fitted with a vigreux column and distilled under nitrogen at atmospheric pressure. With t_{oil} 140 °C, unreacted thionyl chloride was recovered (t_{vap} 75 °C). Heating to t_{oil} 155 °C, delivered the first 5 mL fraction of arsenic trichloride, containing the last traces of thionyl chloride as observed by Raman spectroscopy. This was discarded. No further thionyl chloride was obtained. The vigreux column was removed and the arsenic trichloride distilled at atmospheric pressure under nitrogen at t_{oil} 172 °C to give a colourless liquid (163.1 g, 89%, t_{vap} 131 °C). **Raman data** (glass capillary, cm^{-1}) ν = 409vs (ν_{As-Cl}), 379m ($\beta_{Cl-As-Cl}$), 194m and 159w. **MS** (EI): *m/z* (%) 179.83 (18) [$AsCl_3$], 144.86 (100) [$AsCl_2$].

Triethylarsine [2]

A 500 mL three-necked round bottom flask was equipped with a pressure equalizing dropping funnel and a reflux condenser connected to a schlenk line. Magnesium turnings (8.1 g, 333 mmol) and diethyl ether (100 mL) was added to the flask and a solution of iodoethane (53.0 g, 27.3 mL, 340 mmol) in diethyl ether (30 mL) was added to the dropping funnel. A few millilitres of the C_2H_5I/Et_2O solution was added to the magnesium to begin the reaction. The remaining C_2H_5I/Et_2O solution was added drop wise over one hour. After addition was complete the solution was left to stir for 1.5 hours then brought to reflux for 1 hour. After cooling to room temperature, and then again to –20 °C, a solution of arsenic trichloride (18.1 g, 8.4 mL, 38 mmol) in diethyl ether (50 mL) was added drop wise (*via* the dropping funnel) over one hour. During addition, an orange precipitate formed that was easily broken up with vigorous stirring. After addition was complete the solution was brought to room temperature to stir for 1 hour and brought to reflux for 20 minutes. After cooling again to –20 °C, 1M hydrochloric acid (85 mL) was added cautiously to the reaction mixture. The yellow ether layer was separated and dried over sodium carbonate and filtered. As the ether layer was added to the sodium carbonate it turned colourless. The ether layer was removed *in vacuo* without additional heating and the triethylarsine distilled under a flow of nitrogen (t_{oil} 170 °C, t_{vap} 138 °C) to give a colourless liquid (10.0 g, 62%).

^{1}H NMR: δ_H (500.1 MHz, C_6D_6) 1.26 (6H, q, $^3J_{HH}$ = 7.7 Hz, CH_2), 1.06 (9H, t, $^3J_{HH}$ = 7.7 Hz, CH_3).

^{13}C{^{1}H} NMR: δ_C (125.8 MHz, C_6D_6) 16.4 (s, CH_2), 10.6 (s, CH_3).

Stacked plot of ^{1}H NMR Spectra of Et_3As, 1a and 2a

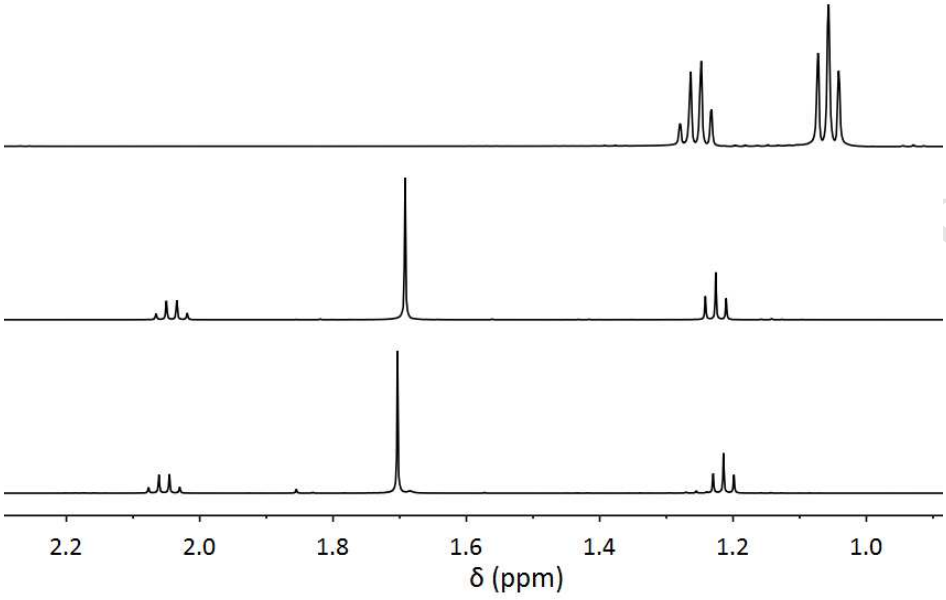

Figure S1: ^{1}H NMR spectra of Et_3As (top), **1a** (middle) and **2a** (bottom) indicating high frequency shift on coordination to the metal fragment.

X-ray Diffraction Details

CCDC 1410325-1410330 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. Table S1 lists details of data collections and refinements.

The crystallographic data for **1a, 1b** and **2a** were collected using a Rigaku SCX mini (Mo-Kα, graphite monochromator) at -100 °C and for **1c**, **2b** and **2c** using a Rigaku XtaLAB (Mo-Kα, confocal optic) equipped with a Dectris P200 at -180 °C diffractometer. (Mo-Kα = λ = 0.71073 Å). Intensity data were collected using ω steps accumulating area detector frames spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz polarisation and long-term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections. Hydrogen atoms on carbon atoms were refined using the riding model. The data for all compounds were collected and processed using *CrystalClear (Rigaku)*.[3] The crystal structures were solved using direct methods and refined by full-matrix least-squares against F^2 (SHELXL) or heavy–atom Patterson methods and expanded using Fourier

techniques.[4] All calculations were performed using the *CrystalStructure* crystallographic software package except for refinement which was performed using *SHELXL–97/2013*.[5] Table S2 lists the details of data collections and refinements. Searches of the Cambridge Structure Database were performed using either *ConQuest* [6] or the *WebCSD*.[7] Images of crystal structures were obtained using *ORTEP-3* [8] with all other manipulations carried out using *Mercury 3.5*.[9]

Table S1: Crystallographic data for compounds **1a–c** and **2a–c**.

	1a	**1b·CH_2Cl_2**	**1c**
Formula	$C_{16}H_{30}AsCl_2Rh$	$C_{29}H_{32}AsCl_4Rh$	$C_{28}H_{30}Cl_2RhSb$
Mr	471.15	700.21	662.11
Colour/Habit	Orange/Prism	Red/Prism	Red/Prism
Crystal Dimensions [mm]	0.30×0.23×0.05	0.33×0.12×0.11	0.20×0.03×0.03
Crystal System	Orthorhombic	Monoclinic	Monoclinic
Space Group	Pbca	$P2_1/n$	$P2_1/n$
***a* [Å]**	47.123(6)	8.5884(7)	8.5871(18)
***b* [Å]**	16.3821(13)	16.9925(14)	32.477(6)
***c* [Å]**	15.0200(12)	19.7897(16)	18.469(4)
α [°]	90	90	90
β [°]	90	92.174(5)	90.501(5)
γ [°]	90	90	90
V [$Å^3$]	11595(2)	2886.0(4)	5150.5(18)
Z	24	4	8
$\rho_{calcd.}$ [g cm^{-3}]	1.619	1.611	1.708
μ [cm^{-1}]	28.482	21.157	19.083
$2\theta_{max}$	50.6	50.7	50.7
Measured refln.	90289	21261	58149
Unique refln.	10438	5159	9265
R [I>2σ(I)]	0.0544	0.0762	0.0368
wR	0.1124	0.2226	0.0827
Largest peak/hole [e $Å^{-3}$]	1.23/-0.64	2.55/-1.28	1.10/-1.06

	2a	**2b**	**2c**
Formula	$C_{16}H_{30}AsCl_2Ir$	$C_{28}H_{30}AsCl_2Ir$	$C_{28}H_{30}Cl_2IrSb$
Mr	560.46	704.59	751.42
Colour/Habit	Orange/Prism	Yellow/Needle	Yellow/Prism
Crystal Dimensions [mm]	0.29×0.07×0.05	0.20×0.02×0.02	0.20×0.02×0.02

Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/c$	$P2_1/n$	$P2_1/n$
***a* [Å]**	13.7804(17)	8.5945(14)	8.6323(17)
***b* [Å]**	32.286(4)	32.182(5)	32.371(8)
***c* [Å]**	8.9519(12)	18.208(4)	18.604(4)
α [°]	90	90	90
β [°]	102.859(7)	90.487(9)	90.598(6)
γ [°]	90	90	90
V [$Å^3$]	3882.9(9)	5035.9(16)	5198(2)
Z	8	8	8
$\rho_{calcd.}$ [g cm^{-3}]	1.917	1.859	1.920
μ [cm^{-1}]	88.536	68.484	63.863
$2\theta_{max}$	50.8	50.8	50.7
Measured refln.	29707	61106	90563
Unique refln.	7062	9247	9415
R [I>2σ(I)]	0.0968	0.0236	0.0214
wR (F^2, all data)	0.2264	0.0527	0.0642
Largest peak/hole [e $Å^{-3}$]	5.16/-3.96	1.22/-1.09	1.49/-1.09

Computational Details

Geometries were fully optimized at the RI-BP86-D3(BJ) level[10] of density functional theory (DFT) including Grimme's three-body dispersion correction[11] with Becke-Johnson damping and auxiliary[12] basis sets for density fitting created automatically in Gaussian (keyword auto). Rhodium, antimony and iridium were described with relativistically adjusted effective core potentials from the Stuttgart-Dresden groups (denoted SDD) with the associated valence basis sets[13] (the Sb basis was augmented with a set of d-polarization functions, exponent 0.211), As was described with the 962(d) all-electron Binning-Curtiss basis,[14] and 6-31G* was used elsewhere. A fine integration grid was used throughout (75 radial shells with 302 angular points per shell). This level is usually a good compromise between accuracy and computational cost for the structures of second-row transition metal complexes.[15] Where available, solid state structures were used as starting points for the optimisations. The nature of the minima was verified by computations of the harmonic frequencies at the same level of theory, which were also used to compute thermodynamic corrections to obtain enthalpies and free energies (at standard pressure and temperature). From test calculations for compound **1a** at the PBE0-D3 level[16] using RI-BP86 and PBE0 optimised structures (see Figure S2 and Table S2) it appeared that binding energies are not very sensitive

to the level of geometry optimisation or energy calculation. Therefore the more economical RI-BP86-D3(BJ) level was employed for all remaining calculations (denoted BP86-D3 for short). WBIs were obtained from natural bond orbital (NBO) analyses at that level.[17] No corrections were made for basis-set superposition error or anharmonicities of vibrational frequencies in the statistical thermodynamic expressions, because these corrections are expected to affect the absolute computed quantities only slightly, and the qualitative trends and general conclusions not at all. All computations were performed using the Gaussian09 suite of programs.[18]

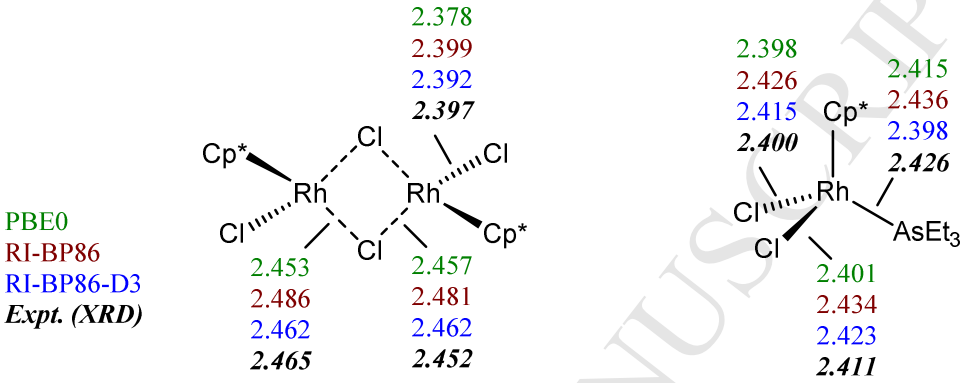

Figure S2: Selected optimised and experimental metal-ligand distances in $[Cp^*RhCl_2]_2$ (left) and $Cp^*Rh(AsEt_3)Cl_2$ (**1a**, right).[19]

Table S2: Computed driving forces [in kJ/mol] as a function of DFT level used in energy calculation and geometry optimisation (SDD/6-31G* basis) for the reaction ½ $[Cp^*RhCl_2]_2$ + $AsEt_3$ → $Cp^*RhCl_2(AsEt_3)$ (**1a**)

Energy //	Geometry[a]	ΔH	ΔG
RI-BP86-D3(BJ)	RI-BP86-D3(BJ)	-82.6	-38.1
RI-BP86-D3[b]	RI-BP86	-76.3	-42.7
PBE0-D3[b]	RI-BP86	-74.3	-40.7
PBE0-D3[b]	PBE0	-78.7	-38.9

[a]Level of energy calculation // level of geometry optimisation; thermodynamic corrections evaluated at the latter level. [b]-D3 single points without BJ damping.

Cartesian Coordinates (xyz format in Å) of all Compounds of this study, RI-BP86-D3(BJ) Optimized.

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$[Cp^*RhCl_2]_2$

Rh -0.1460225693 -0.2914136378 1.7491111932

Cl 0.7360096505 -1.5228049877 -0.1916163686

Cl -2.2928509241 -1.2799285994 1.3828885435

C 1.8133602 -0.2867250793 2.6827438653

C 1.209631869 1.0093823113 2.8359832503

C -0.0567758959 0.8403294793 3.5639985787

C -0.1980680778 -0.5696124419 3.8868859713

C 0.930882277 -1.2815192469 3.3097838703

C 3.1038262774 -0.5544142641 1.9709247282

C 1.7790375225 2.2908359858 2.3092703531

C -0.9983605992 1.9405037669 3.9489902026

C -1.3218299668 -1.1894626494 4.658616689

C 1.1878230458 -2.755574542 3.3881305532

Cl -0.7360096505 1.5228049877 0.1916163686

Rh 0.1460225693 0.2914136378 -1.7491111932

Cl 2.2928509241 1.2799285994 -1.3828885435

C -1.8133602 0.2867250793 -2.6827438653

C -1.209631869 -1.0093823113 -2.8359832503

C 0.0567758959 -0.8403294793 -3.5639985787

C 0.1980680778 0.5696124419 -3.8868859713

C -0.930882277 1.2815192469 -3.3097838703

C -3.1038262774 0.5544142641 -1.9709247282

C -1.7790375225 -2.2908359858 -2.3092703531

C 0.9983605992 -1.9405037669 -3.9489902026

C 1.3218299668 1.1894626494 -4.658616689

C -1.1878230458 2.755574542 -3.3881305532

H 1.0463073731 1.2681462211 -5.7281519787

H 1.5545181786 2.1968703528 -4.2794828887

H 2.2408017646 0.5886833284 -4.5770499825

H 1.0076478212 -2.7331432799 -3.1829068056

H 0.6984679319 -2.3968866016 -4.9124980461

H 2.0276398989 -1.5606476699 -4.0515572256

H -2.1599512575 -2.152444749 -1.2817825409

H -2.6115723446 -2.6307969158 -2.9554287031

H -1.0178050453 -3.0853030648 -2.2767085291

H -3.1723303078 -0.0530242263 -1.0514287893

H -3.1872472705 1.6117669718 -1.6762578967

H -3.9592291712 0.3053315976 -2.6287283485

H -1.698608511 3.1121355531 -2.4783773232

H -0.243699096 3.3152296455 -3.4847537945

H -1.8270231829 2.9992099532 -4.2591844119

H 2.6115723446 2.6307969158 2.9554287031

H 2.1599512575 2.152444749 1.2817825409

H 1.0178050453 3.0853030648 2.2767085291

H 3.1872472705 -1.6117669718 1.6762578967

H 3.1723303078 0.0530242263 1.0514287893

H 3.9592291712 -0.3053315976 2.6287283485

H 0.243699096 -3.3152296455 3.4847537945

H 1.698608511 -3.1121355531 2.4783773232

H 1.8270231829 -2.9992099532 4.2591844119

H -1.5545181786 -2.1968703528 4.2794828887

H -1.0463073731 -1.2681462211 5.7281519787

H -2.2408017646 -0.5886833284 4.5770499825

H -0.6984679319 2.3968866016 4.9124980461

H -1.0076478212 2.7331432799 3.1829068056

H -2.0276398989 1.5606476699 4.0515572256

23

$AsEt_3$

As 1.6774328635 0.1845711569 0.0450861399

C 3.053877761 -0.0521769726 -1.3983161376

H 2.8035917545 0.6792287319 -2.1880952658

H 4.0499378062 0.2204695741 -1.0036582232

C 3.0504342688 -1.4778120705 -1.9664948217

H 2.0474321959 -1.7625121562 -2.3333428126

H 3.3451768986 -2.2176887946 -1.2004559702

H 3.757070986 -1.5761279331 -2.8114705353

C 2.3950978928 1.9064909927 0.7814491364

H 1.9389299064 2.0425863925 1.7795158348

H 3.486903057 1.8171080686 0.9248655799

C 2.0598547009 3.0942314831 -0.1330586088

H 0.9706731767 3.1806241716 -0.2982601091

H 2.5384138458 2.9894322657 -1.1236357934

H 2.4109621925 4.047700485 0.303552253

C 2.4624036002 -1.0692954191 1.4115345792

H 1.8861128385 -0.8857573562 2.3376035013

H 2.189972412 -2.0870407992 1.076111916

C 3.9684818891 -0.9708801924 1.6798683694

H 4.2595400217 0.0398225448 2.0163834151

H 4.5604380692 -1.2060860495 0.7778045356

H 4.2765078624 -1.6827871236 2.4690240171

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Compound **1a**

Rh 12.5378317835 8.3573068503 3.5942883934

As 13.9572357241 9.9340294153 2.4767243677

Cl 14.2447562639 8.296420435 5.3009138151

Cl 11.4237653473 10.3228003955 4.46980585

C 11.7958345164 6.294907749 4.1243249737

C 10.668040498 7.1256401267 3.8481135531

C 10.8097324492 7.6541649185 2.4848369527

C 12.0088743012 7.0766149336 1.9129424252

C 12.6627416715 6.2858143814 2.9403440776

C 12.1130757532 5.5756609264 5.3991313419

H 12.1965613319 4.48745658 5.2198333557

H 11.3377427383 5.7440565083 6.162910677

H 13.0753502105 5.93820558 5.8069087502

C 9.534877104 7.4658193581 4.765142424

H 9.6779939421 7.0292911372 5.7660811601

H 8.5783822216 7.0919410323 4.3537339612

H 9.4597032319 8.5630650259 4.8803249746

C 9.8032257739 8.526477679 1.7969407134

H 8.8963294208 7.9519294673 1.5248281207

H 10.2188699815 8.9619843445 0.8733672628

H 9.5044261058 9.3572079733 2.459197057

C 12.4248128778 7.1764876714 0.4743398907

H 11.8527246955 6.4489280737 -0.1334284613

H 13.4945800324 6.9470695457 0.3439180502

H 12.2320791369 8.17898303 0.0563869138

C 13.9060225955 5.4587082262 2.8098295652

H 14.4955072665 5.7534734542 1.9263670877

H 13.6599865545 4.3832690602 2.7096905229

H 14.5418023912 5.5834203815 3.7033496672

C 15.083130948 11.1306660645 3.5775646117

H 15.7184323856 10.4446450804 4.160992898

H 15.7219696542 11.6749902362 2.8563918817

C 14.3245091164 12.077543164 4.5082484445

H 13.7374992279 11.5048594061 5.2420260008

H 13.6244465434 12.7315147306 3.9597786719

H 15.0447217588 12.7208569541 5.0472390788

C 15.3574335182 9.1772405104 1.2929948875

H 14.8438925555 8.5715522153 0.5273742458

H 15.8437591923 10.0220905356 0.7714602122

C 16.3763951153 8.342276727 2.0809075743

H 15.8763019806 7.5955640927 2.7201405527

H 16.9847643758 8.97709698 2.7471647366

H 17.0660532724 7.8168896377 1.3950473074

C 12.9505927371 11.1519878319 1.2840500804

H 12.5411948008 10.5217272405 0.4731000894

H 12.1004042198 11.4865997758 1.9026064221

C 13.7617737707 12.3272149758 0.7261484212

H 14.6279705961 11.9879664157 0.1302023709

H 14.1409295003 12.9725084671 1.5371637738

H 13.1322888099 12.9544146979 0.068510295

34

PPh_3

P 0. 0. -1.5942475165

C 1.5921534603 -0.4370399501 -0.7568473914

C 2.3485831197 -1.4859986151 -1.3239048087

C 2.079515834 0.2093188005 0.3980098224

C 3.556332627 -1.8929980477 -0.7396394436

C 3.2952955803 -0.1910222844 0.9748196425

C 4.0340803137 -1.2435107663 0.4108426687

H 1.9840159661 -1.9851892517 -2.2302232169

H 1.5033465497 1.0269077098 0.8443487065

H 4.1308230097 -2.7115709839 -1.1879162807

H 3.6647570776 0.3202894437 1.8712271875

H 4.9826041972 -1.553739379 0.8634234002

C -0.4175890309 1.5973653184 -0.7568473914

C -1.1745644294 -1.1603253683 -0.7568473914

C 0.1126209908 2.7769319521 -1.3239048087

C -2.4612041105 -1.290933337 -1.3239048087

C -1.2210333157 1.6962541396 0.3980098224

C -0.8584825183 -1.90557294 0.3980098224

C -0.1387819149 4.0263734231 -0.7396394436

C -3.4175507121 -2.1333753754 -0.7396394436

C -1.4822176392 2.9493208277 0.9748196425

C -1.8130779411 -2.7582985433 0.9748196425

C -0.9401282434 4.1153714158 0.4108426687

C -3.0939520703 -2.8718606495 0.4108426687

H 0.7272163403 2.710802854 -2.2302232169

H -2.7112323063 -0.7256136023 -2.2302232169

H -1.6410014388 0.7884824479 0.8443487065

H 0.1376548891 -1.8153901576 0.8443487065

H 0.2828778514 4.9331831569 -1.1879162807

H -4.4137008611 -2.221612173 -1.1879162807

H -2.1097573335 3.013628006 1.8712271875

H -1.554999744 -3.3339174497 1.8712271875

H -1.1457243255 5.0919315013 0.8634234002

H -3.8368798716 -3.5381921223 0.8634234002

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Cp*Rh(PPh_3)Cl_2

C 2.6198668333 2.5869995417 5.7892261646

C 2.7002967689 2.8206147902 7.2313500534

C 1.7557203809 1.917219784 7.8725599899

C 1.0336804211 1.2195382417 6.8354317189

C 1.5922738416 1.6272393242 5.5402688104

C 3.4717282131 3.2901591504 4.7798754474

H 3.3227052401 4.3826846662 4.8562617416

H 3.2172988115 2.9878904259 3.7521276148

H 4.5397568573 3.0653725859 4.9588191994

C 3.7213761661 3.6904026816 7.8994278005

H 3.4496296109 3.9076776531 8.9442584512

H 3.8124829554 4.6540360105 7.3709878826

H 4.7158844077 3.2019498986 7.8962786462

C 1.639184289 1.6510558298 9.3429496482

H 0.5889549538 1.5138246659 9.649319252

H 2.0639910264 2.4773905912 9.9324578977

H 2.1955108842 0.7294097628 9.6011299645

C 0.0116412551 0.1379804688 7.0102697934

H -0.8610093905 0.3279023189 6.3602489291

H -0.3347402456 0.0734508296 8.0541672625

H 0.4401449171 -0.8442926667 6.7316922179

C 1.1194831108 1.1056992906 4.2187593629

H 1.6136584937 1.6214163411 3.3803542939

H 0.0296338072 1.2647962846 4.119655534

H 1.3221525178 0.0216052525 4.1299342226

C -1.2863789426 6.0880221575 7.9529083105

C -1.3510021202 7.1411545808 8.8898570279

H -0.7435622917 7.1087926832 9.8000910187

C -2.1764077528 8.2485455512 8.6467574935

H -2.2170706163 9.0647638499 9.376948955

C -2.9384695404 8.3122835193 7.4694786183

H -3.5796021159 9.1802246363 7.2780078321

C -2.8694488128 7.2662705968 6.5355694298

H -3.4522390916 7.3155324253 5.6092085537

C -2.0465529649 6.1553624127 6.7696464496

H -1.9807538442 5.3436497603 6.0395908278

C 1.0223909231 5.2637798697 9.4298120142

C 1.3069323622 4.7558578391 10.7130609896

H 0.6800033919 3.9680047576 11.141301127

C 2.388481126 5.265439203 11.4516762118

H 2.6007686559 4.8626658268 12.4484278941

C 3.1864846745 6.2899827875 10.9195327577

H 4.0273680492 6.6880673074 11.4981320642

C 2.9010648066 6.8045773863 9.6425930635

H 3.5214853563 7.6026595156 9.2199915506

C 1.8314764405 6.2936305212 8.8961781952

H 1.6284644928 6.6633371764 7.884696208

C -1.411374475 3.6296771335 9.4381168054

C -1.9023966721 2.3869677234 8.9932053791

H -1.6292440917 2.0391962016 7.9924854537

C -2.77343786 1.6422463025 9.803910874

H -3.1568853864 0.6801067474 9.446186303

C -3.1626152565 2.1346305006 11.059303967

H -3.8396080375 1.5516376802 11.6936340173

C -2.6988477965 3.3881894953 11.4942109629

H -3.0172064081 3.7865647948 12.4640475302

C -1.834412491 4.1384900832 10.6847453301

H -1.4924744394 5.1229746209 11.0202087414

Cl 1.0283985051 5.4848701384 5.535017847

Cl -1.4689260941 3.00970267 5.5474334121

P -0.2906744872 4.5865443437 8.3349813463

Rh 0.6659966779 3.3759634772 6.636243538

34

$AsPh_3$

As 0.003100692364 0.017605514856 -1.292218673535

C 1.339037698862 1.092884525047 -0.308038890810

C 1.645398477782 2.368224511836 -0.823668068602

C 2.568677116679 3.197203686595 -0.167792882782

C 3.201702239806 2.752912530560 1.004571346417

C 2.905964817438 1.480010485731 1.518710122308

C 1.977270460512 0.651793261282 0.867253350637

C -1.612365084753 0.617821819106 -0.324911955660

C -1.572583514039 1.304606355739 0.903608172899

C -2.766304515124 1.677010897758 1.542546306961

C -4.006696197133 1.366313705264 0.962136022037

C -4.052231305691 0.684823014642 -0.264737451113

C -2.859606747165 0.317150285444 -0.907615367207

C 0.282058722403 -1.693961163299 -0.341258867822

C -0.521642931628 -2.130256450368 0.729272063176

C -0.258355868318 -3.361115902566 1.353625383169

C 0.809417010529 -4.162147658330 0.918168254414

C 1.613774721193 -3.732184458370 -0.151193714916

C 1.346179420213 -2.508147783546 -0.782431132835

H 1.157944698270 2.716679187392 -1.742925377986

H 2.797886102492 4.188659460272 -0.575129852131

H 3.927079429279 3.396822615620 1.514551176472

H 3.398337644138 1.129348631499 2.433220134665

H 1.745740639710 -0.338926203619 1.272888669028

H -0.607583229709 1.545623496104 1.362043665274

H -2.726406193815 2.210550763356 2.499199899343

H -4.936562187330 1.658285276182 1.463124788011

H -5.017193492625 0.442945528330 -0.724432214679

H -2.899569122283 -0.209888687783 -1.869066130016

H -1.350139072751 -1.506130586603 1.080975695406

H -0.889213838604 -3.691855797490 2.187469583975

H 1.013846791576 -5.120706145997 1.408280980696

H 2.448291549715 -4.353439277093 -0.497449619145

H 1.975094400232 -2.179844018164 -1.620250578095

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Compound **1b**

Rh 6.4720973756 11.8955967735 13.7223435935

As 7.4732699843 13.2375763752 12.0118483878

Cl 6.1241177247 13.9939385653 14.8567239355

Cl 8.6520452957 11.5365468461 14.7177409169

C 6.1159880093 9.7630755392 13.40625901

C 5.3860228816 10.516903264 12.4129987438

C 4.4440561618 11.3850124371 13.1072941508

C 4.53981084 11.0807857814 14.535088566

C 5.5730200188 10.1075508527 14.7256599247

C 7.1519418221 8.7073514868 13.1659584661

C 5.5101950188 10.3530952505 10.9275361967

C 3.4310762595 12.304034574 12.4938791417

C 3.7024546705 11.7363159778 15.5880262799

C 6.0637596891 9.5257868189 16.015123785

C 8.6306280713 12.2830833127 10.7605979015

C 9.1392805952 11.0347350206 11.1634203937

C 9.9923043484 10.320058583 10.3071438058

C 10.3388778303 10.8505122515 9.0539398815

C 9.8476588718 12.1076575647 8.6626627486

C 8.9987635342 12.8292707657 9.5163655466

C 6.0917361049 14.0352133347 10.8877865501

C 5.7864950994 13.5760476124 9.5926398832

C 4.6866892076 14.1114193937 8.8997470952

C 3.8961284431 15.1080007458 9.493509955

C 4.2082579418 15.5738050014 10.7826696802

C 5.2991107843 15.0395728972 11.4829878464

C 8.5365018455 14.8079946864 12.4730793086

C 8.6152132891 15.8788686679 11.5636042418

C 9.4225201247 16.9866976276 11.8650116449

C 10.1430838684 17.0231360142 13.0695918136

C 10.0550089286 15.9520128356 13.9736952245

C 9.25109139 14.8393429554 13.6828208852

H 8.8961437454 10.6559293083 12.1621663098

H 10.3955483769 9.3523370297 10.6262857091

H 11.0031799032 10.2914563871 8.3855839011

H 10.1309353973 12.5315748995 7.6926295394

H 8.6304927786 13.8158625432 9.2150605184

H 6.4053390466 12.8061474026 9.1198991054

H 4.4523570726 13.7494766083 7.8922069065

H 3.0390867771 15.5231070621 8.9516884138

H 3.5939115984 16.3513581002 11.2502224547

H 5.5259008773 15.3735452818 12.5020822586

H 8.035963824 15.8617349136 10.634052606

H 9.4814240491 17.8236578293 11.1598698871

H 10.7690149294 17.8910565266 13.3061169906

H 10.608477348 15.9824625334 14.9187417398

H 9.1684065758 14.0047213553 14.3859520923

H 6.7358738204 7.7022346678 13.3726352619

H 8.0192916998 8.8650122726 13.8310263425

H 7.5059999563 8.7209105854 12.1226764726

H 4.8988399484 9.4927609298 10.5928789447

H 6.5539945293 10.1690370305 10.6226124992

H 5.1506225642 11.2476971442 10.3956860841

H 2.4309349039 11.8279026805 12.4689896828

H 3.7029772846 12.5829575849 11.4635722583

H 3.3524713481 13.2347849209 13.0801283013

H 2.6309696539 11.5321288189 15.4053584982

H 3.86206501 12.8300810604 15.5690885165

H 3.9608210627 11.3756763263 16.5958570513

H 5.8428576526 8.4426970625 16.0663400363

H 5.5972624353 10.0167901114 16.8836843935

H 7.1579798 9.66161121 16.0967417199

34

$SbPh_3$

Sb 0.000637198078 0.001370123647 -1.351161359811

C -0.496100225429 -1.781303711702 -0.205671632435

C -1.224965526385 -1.724393960410 0.999276258366

H -1.588664466543 -0.760615976488 1.372754452220

C -1.483661526637 -2.897401496705 1.727784379513

H -2.050257369365 -2.841768788534 2.664640910485

C -1.017961479658 -4.136785623968 1.259857876833

H -1.220403826865 -5.050616871471 1.829884023771

C -0.294397249012 -4.202915198251 0.058225582939

H 0.070789530948 -5.167980461845 -0.311699826481

C -0.038034581729 -3.030741194380 -0.671947423827

H 0.528757261534 -3.095948450103 -1.609648057062

C 1.791445965747 0.462340597537 -0.203330408384

C 2.107854112320 -0.199485899424 1.000029001380

H 1.455780143314 -0.997121906736 1.373432448676

C 3.254531761326 0.161511578496 1.727293057360

H 3.490991603629 -0.358699329613 2.662844309689

C 4.094766460407 1.184957577829 1.259980608107

H 4.988963471656 1.464650566409 1.828503956666

C 3.789021389260 1.846370138246 0.059738644164

H 4.442695097158 2.644541266372 -0.310515490502

C 2.644880999247 1.483582374631 -0.669530169612

H 2.417976849540 2.007394442931 -1.607055401305

C -1.295551689020 1.320654600487 -0.203311642366

C -0.882008280430 1.929075083660 0.998575596111

H 0.135817809706 1.764931023361 1.369905593072

C -1.771130362271 2.738750301142 1.725184000902

H -1.440274833775 3.207122530533 2.659496808497

C -3.079164642196 2.947060928104 1.258627953742

H -3.771325483415 3.578673372764 1.826913297483

C -3.497518370725 2.347838808654 0.059442094263

H -4.516916799838 2.508812178753 -0.309927711112

C -2.607838676830 1.542007808815 -0.669433645169

H -2.946030263540 1.079957567146 -1.605956086176

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Compound **1c**

Sb 4.3902125473 8.7645255891 11.7350019955

Rh 3.259329434 9.656135425 9.6443479768

Cl 5.4725026676 9.6970543898 8.6496754135

Cl 2.9183824466 7.3016364833 9.1911012889

C 2.3750904123 11.1775583774 8.2625920658

C 1.3498424639 10.2490897906 8.6335808193

C 1.2287025525 10.2524026797 10.094642549

C 2.1495134465 11.2566068511 10.6089798874

C 2.8965172921 11.7920830981 9.4892270162

C 2.8989018503 11.4731324092 6.8906071031

H 2.7156096815 12.5299808181 6.6194277128

H 2.4252629489 10.8328113079 6.1298828779

H 3.9892111276 11.2910690519 6.8563042277

C 0.5524926577 9.363945169 7.7258784743

H 0.8519927453 9.4895911627 6.6735166616

H -0.5257249903 9.5945338024 7.8125390149

H 0.7056824564 8.3027526833 7.9963062596

C 0.2399647647 9.4444427963 10.8805794738

H -0.7627000782 9.9153484171 10.867074743

H 0.5550653352 9.3335487356 11.9311441766

H 0.152139111 8.4316778015 10.4526326411

C 2.2505220728 11.7152043417 12.0346656065

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H 1.9143601042 10.9316028431 12.7331282651

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C 1.6375831687 8.6430652695 15.2358880336

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C 0.8383194839 7.5234826772 14.954784023

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C 5.7566632037 6.2415012019 12.8513046725

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C 6.5563226117 5.0875564725 12.8228745851

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C 7.175895759 4.6931834196 11.6258521709

H 7.7965991909 3.7901576059 11.6047079192

C 6.9958713523 5.4486090345 10.4554267101

H 7.4728419454 5.1354824295 9.5199849945

C 6.1982414109 6.6038381159 10.4720342861

H 6.0443058961 7.1912499279 9.5603587658

56

$[Cp^*IrCl_2]_2$

Ir -0.1217306022 -0.2996545291 1.8218406339

Cl 0.725709306 -1.4767644401 -0.1916328726

Cl -2.2696831693 -1.2968248234 1.3897968366

C 1.8380435341 -0.2939302691 2.7562475567

C 1.2311312857 1.0075795442 2.9053544451

C -0.0390031829 0.8400685058 3.6391611877

C -0.1820819094 -0.5751907458 3.9613454816

C 0.9539098722 -1.292086941 3.3893404028

C 3.1283392091 -0.5708449933 2.0462879142

C 1.7915856935 2.2913135701 2.3723591829

C -0.9715341457 1.9424117543 4.0419364251

C -1.3101296832 -1.1947368971 4.7280077289

C 1.2209592349 -2.7631621821 3.496594022

Cl -0.725709306 1.4767644401 0.1916328726

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62

$Cp^*Ir(PPh_3)Cl_2$

C 5.4137981483 14.1535595029 2.7995019062

C 4.4609158793 13.2463090899 3.4389018876

C 4.5485220673 13.4749794609 4.8844904943

C 5.5799331611 14.4331329241 5.1383088722

C 6.1454198944 14.8454344656 3.8418281566

C 5.5199300895 14.4268695402 1.3294300581

H 4.9254757128 15.3247720714 1.0732146249

H 5.1296678994 13.5830861953 0.7406783571

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C 3.4194334325 12.406432815 2.7634926265

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C 6.0587456814 14.9418761627 6.4634661357

H 5.8171458486 16.0150167587 6.5818235223

H 7.1543971154 14.8195509345 6.5419271525

H 5.5993559276 14.3881426101 7.2973536439

C 7.163726825 15.9323177353 3.6731948694

H 6.7260412997 16.9144312699 3.9366214403

H 7.5240033425 15.9889447742 2.6335845942

H 8.0293669839 15.7516779712 4.3346570851

C 8.4510581775 9.9762925814 2.6601453895

C 9.2200328693 9.8931665208 3.8368763272

H 9.1639392414 10.6962247904 4.5770631111

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C 9.3307094849 7.8214627604 1.9352184023

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C 8.5064698562 8.9336431699 1.7110231563

H 7.8930562082 8.9787291677 0.8051569096

C 8.5848224249 12.4504244705 1.2113725374

C 9.0753112892 13.6877478491 1.6711692034

H 8.7919080192 14.0262459778 2.6721970653

C 9.9543656521 14.4376490202 0.8741659894

H 10.3379386433 15.3952919619 1.2436992177

C 10.3512229402 13.9557864061 -0.3829939372

H 11.0340470664 14.5430177624 -1.0070831013

C 9.8880668886 12.707197683 -0.832517587

H 10.2127696273 12.3170906437 -1.8035984488

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H 3.1312238105 9.404877675 -0.8585869677

C 4.7846261312 10.8104806887 -0.8228910868

H 4.5801379382 11.203547074 -1.8251347344

C 5.8690619393 11.3176723762 -0.0858578683

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Cl 8.6556363941 13.0101637296 5.1346121732

Cl 6.1862296686 10.564807104 5.1566912374

Ir 6.5059548237 12.6850378009 4.0124623891

P 7.4591301865 11.4868873964 2.302007049

62

Compound **2b**

Ir 0.8312993898 0.9975702838 5.8247121923

As 0.2975228452 0.4994313627 3.5339219471

Cl -0.0626439007 -1.1753272587 6.5070498871

Cl -1.390389541 1.9907916556 5.9081996444

C 2.8246393844 0.6057968979 6.634332676

C 2.0387144253 1.2468901869 7.7022119635

C 1.64842874 2.5501691439 7.2413063299

C 2.1528384304 2.7398825456 5.8777533346

C 2.9276064847 1.5462723049 5.5348887209

C 3.5089483352 -0.7216035486 6.7631248554

C 1.7143647653 0.5974271068 9.01256407

C 0.8188509893 3.5588856684 7.973310151

C 2.0455401613 4.0070050399 5.0833849386

C 3.7695862785 1.3658292395 4.3069598318

C 1.3535190853 -0.9283775653 2.7252457542

C 1.39518772 -1.126933037 1.3323888073

C 2.1547835413 -2.1815139435 0.8025238726

C 2.8584465341 -3.0439458275 1.6605568061

C 2.7916935335 -2.8608241924 3.0513172314

C 2.0385078384 -1.8037854236 3.5868731327

C -1.5247359571 0.0393970231 3.0077111882

C -2.3650249574 -0.6301136217 3.9141675633

C -3.6526918778 -1.0071316758 3.5036757008

C -4.0992971686 -0.7173684439 2.2040879031

C -3.2561923619 -0.0443034638 1.3053288679

C -1.9661640352 0.3376444569 1.7052146966

C 0.6302123882 2.0586244815 2.409795377

C -0.2331838386 3.1597565103 2.5924314892

C 0.0088964556 4.3563801646 1.9029626979

C 1.1128644227 4.4660617621 1.0391229091

C 1.9707681876 3.3701640464 0.8572407307

C 1.7293636933 2.1637785192 1.5378535983

H 4.3518825894 -0.6564971767 7.4778411082

H 3.9107549284 -1.0602743172 5.7947071621

H 2.8010496072 -1.4844462424 7.1309326625

H 0.9889962315 1.1932908889 9.5886936551

H 2.6273549977 0.4720600135 9.6247276401

H 1.2686213405 -0.3991337143 8.8407279599

H 1.4072571003 4.4779306439 8.152068554

H 0.4712644956 3.1705128275 8.9431426844

H -0.0743524166 3.8175318381 7.3772463799

H 2.1774128884 3.8209447517 4.0058312987

H 2.8116162749 4.7408097906 5.4028483886

H 1.0525266259 4.4653626079 5.2206487748

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H -1.3181251489 0.8830683165 1.0104392496

H -1.0735359725 3.0804480855 3.2923758352

H -0.6625850578 5.2099805024 2.0481541189

H 1.3027533653 5.4049190077 0.5072574177

H 2.8293529524 3.4488933131 0.1807357936

H 2.3954392089 1.3079819629 1.3841405227

62

Compound **2c**

Ir 3.2467208313 1.0610728185 15.3638967146

Sb 3.8642566954 0.5264632326 12.9365436655

Cl 5.4092852211 2.2028460532 15.368393893

Cl 4.311180313 -1.0590935733 15.97256499

C 2.3380878208 2.5195827593 16.8112510905

C 1.9764292269 1.1865805231 17.2082983232

C 1.2588949353 0.5547696205 16.0885853967

C 1.1577425827 1.5355962801 15.0190685823

C 1.8722729533 2.7422548728 15.4362979994

C 3.1150023991 3.5238684825 17.6061283458

H 3.4525285325 3.104810905 18.5669303977

H 2.4935468087 4.4152270127 17.8116792772

H 4.0129240601 3.841049878 17.0452636098

C 2.2879847902 0.4939907866 18.5000816295

H 1.3589051282 0.263959957 19.0547205212

H 2.9323190575 1.1126668001 19.1443149897

H 2.8200420706 -0.4548218943 18.3027580106

C 0.631261499 -0.8053814747 16.1402971283

H -0.2466565799 -0.8065160099 16.8149123995

H 1.3567815012 -1.5481409204 16.5147199618

H 0.2936357158 -1.1269793685 15.1421546388

C 0.3819578039 1.3705467329 13.7448740327

H 0.7734873583 2.0282915197 12.9516245441

H -0.6793736217 1.6372971434 13.9116988711

H 0.4203652275 0.3305296584 13.3794904368

C 1.9817162562 4.0307810199 14.6767357017

H 1.1593848769 4.72334097 14.9435739407

H 1.9480316516 3.8572073021 13.5885624814

H 2.9392030876 4.5289516758 14.9014514979

C 5.8798834153 0.1146661613 12.3675688125

C 6.2938660548 0.3839896645 11.0497748323

H 5.6018166841 0.8365339188 10.3294911053

C 7.6119074306 0.0910586334 10.6643011408

H 7.940218048 0.3023432552 9.6401515671

C 8.5069088971 -0.4642061104 11.5933169438

H 9.5362496923 -0.6892286105 11.2917001524

C 8.0886277757 -0.7239074235 12.9088630443

H 8.7906259394 -1.1479913124 13.6354483327

C 6.7732615296 -0.4348555187 13.3055435779

H 6.4451198514 -0.6230458061 14.3337787501

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C 2.1255566013 -1.9792397232 12.959662354

H 2.2802934435 -1.8595691856 14.0387656958

C 1.3597572296 -3.0453385702 12.4603676723

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C 4.1946194573 3.3509287253 11.8497433435

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References

1. K. S. Pandey, A. Steiner, W. H. Roesky, S. Kamepalli, A. H. Cowley, *Inorg. Synth.* 1997, **31**, 148-150.
2. W. A. Herrmann, H. H. Karsch, *Synthetic Methods of Organometallic and Inorganic Chemistry Vol 3: Phosphorus, Arsenic, Antimony and Bismuth, Vol. 3*, Thieme, New York, **1996**.
3. (a) CrystalClear 2.0, Rigaku Corporation, 2007; (b) CrystalClear Software User's Guide, Molecular Structure Corportation ©, 2007; (c) J. W. Pflugrath, *Acta Crystallogr. Sect. D. Biol. Crystallogr.* 1999, **55**, 1718-1725.
4. (a) A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* 1999, **32**, 115-119; (b) P. T. Beuerskens, G. Admiraal, G. Beuerskens, W. P. Bosman, R. de-Gelder, R. Israel, J. M. M. Smits, The DIRDIF-99 program system, Technical Report of the Crystallogrpahy Laboratory, University of Nijmegen, The Netherlands, 1999; (c) P. T. Beuerskens, G. Admiraal, H. Behm, G. Beuerskens, J. M. M. Smits, C. Smykalla, *Z. Kristallogr* 1991, Suppl 4, 99.
5. (a) *CrystalStructure 3.8.1: Crystal Structure Analysis Package, Rigaku and Rigkau/MSC (2000-2006) 9009 New Trails Dr. The Woodlands, TX 77381 USA*; (b) *CrystalStructure 4.0: Crystal Structure Analysis Package, Rigaku Corporation (2000-2010). Tokyo 196-8666, Japan*; (c) G. M. Sheldrick, *Acta Crystallogr A* 2008, **64**, 112-122.
6. I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson, R. Taylor, *Acta Crystallogr. Sect. B-Struct. Sci.* 2002, **58**, 389-397.
7. I. R. Thomas, I. J. Bruno, J. C. Cole, C. F. Macrae, E. Pidcock, P. A. Wood, *J. Appl. Crystallogr.* 2010, **43**, 362-366.
8. L. Farrugia, *J. Appl. Crystallogr.* 2012, **45**, 849-854.
9. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *J. Appl. Crystallogr.* 2008, **41**, 466-470.
10. (a) A. D. Becke, *Phys. Rev. A* 1988, **38**, 3098-3100; (b) J. P. Perdew, *Phys. Rev. B* 1986, **33**, 8822-8824; (c) J. P. Perdew, *Phys. Rev. B* 1986, **34**, 7406-7406.
11. (a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* 2010, **132**, 154104; (b) T. Risthaus, S. Grimme, *J. Chem. Theory Comput.* 2013, **9**, 1580-1591; (c) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* 2011, **32**, 1456-1465.
12. (a) A. D. Becke, E. R. Johnson, *J. Chem. Phys.* 2005, **122**, 154104; (b) E. R. Johnson, A. D. Becke, *J. Chem. Phys.* 2006, **124**, 174104.
13. (a) P. Schwerdtfeger, M. Dolg, W. H. E. Schwarz, G. A. Bowmaker, P. D. W. Boyd, *J. Chem. Phys.* 1989, **91**, 1762-1774; (b) A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, *Mol. Phys.* 1993, **80**, 1431-1441.
14. R. C. Binning, L. A. Curtiss, *J. Comput. Chem.* 1990, **11**, 1206-1216.
15. M. P. Waller, H. Braun, N. Hojdis, M. Bühl, *J. Chem. Theory Comput.* 2007, **3**, 2234-2242.
16. (a) C. Adamo, V. Barone, *J. Chem. Phys.* 1999, **110**, 6158-6170; (b) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77**, 3865-3868.
17. A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* 1988, **88**, 899-926.
18. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford, CT, USA, **2009**.
19. [Cp*RhCl2]2 (CSD refcode CLCPRH) taken from: M. R. Churchill, S. A. Julis, F. J. Rotella, Inorg. Chem. 1977, 16, 1137-1141; 1a: this work.