

Iridium–Ruthenium Cluster Complexes with SnPh₃ Ligands from the Reaction of IrRu₃(CO)₁₃(μ-H) with HSnPh₃

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Abstract The reaction of IrRu₃(CO)₁₃(μ-H), **1** with HSnPh₃ in hexane solvent at reflux has provided the new mixed metal cluster compounds Ir₂Ru₂(CO)₁₁(SnPh₃)(μ-H)₃, **2** and IrRu₃(CO)₁₁(SnPh₃)₃(μ-H)₄, **3** containing SnPh₃ ligands. Compound **2** which was obtained in low yield (3%) contains one SnPh₃, two iridium atoms and two ruthenium atoms. The increase in the number of iridium atoms must have resulted from a metal–metal exchange process. The major product **3** (19% yield) contains an open cluster of one iridium and three ruthenium atoms with three SnPh₃ ligands and four hydride ligands. Both compounds were characterized structurally by single crystal X-ray diffraction analysis.

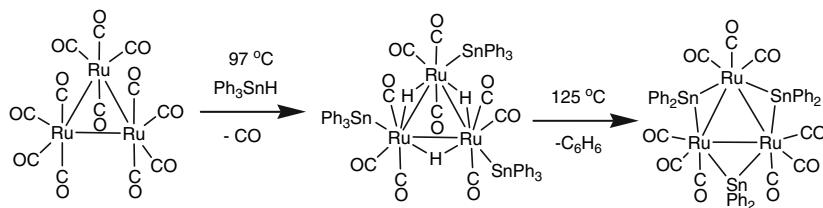
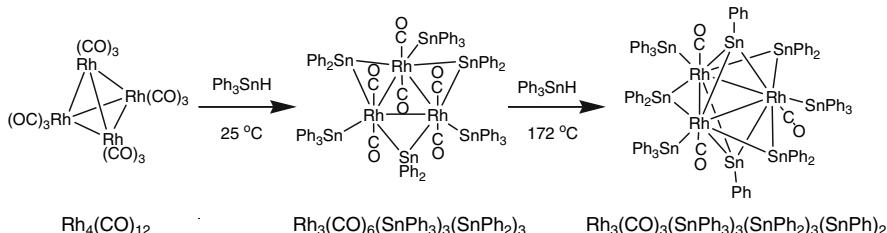
Keywords Ruthenium · Iridium · Tin

Introduction

Tin is well-known to be an effective modifier of transition metal catalysts [1–13]. Recent studies have shown that polynuclear metal carbonyl cluster complexes containing tin ligands can serve as effective precursors to multimetallic heterogeneous catalysts that exhibit high activity and improved selectivity for certain types of catalytic hydrogenation reactions [10–13]. We have recently shown that the phenylstannanes, HSnPh₃ and H₂SnPh₂, are good reagents for introducing phenyltin ligands into polynuclear metal carbonyl cluster complexes, see Schemes 1 [14] and 2 [15].

Dedicated to Professor Malcolm H. Chisholm on the occasion of his 65th birthday.

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**Scheme 1****Scheme 2**

Bridging SnPh₂ and SnPh ligands are often formed by cleavage of phenyl groups from the SnPh₃ ligands by mild heating. In some cases, the number of tin ligands that can ultimately be added to a complex is quite large. For example, the complexes Ru₅(CO)₁₀(SnPh₃)(μ-SnPh₂)₄(μ₅-C)(μ-H), [16] Ru₄(CO)₈(μ-SnPh₂)₄(μ₃-SnPh)₂ [10] and Rh₃(CO)₃(SnPh₃)₃(μ-SnPh₂)₃(μ₃-SnPh)₂ [15] contain five, six and eight tin ligands, respectively.

Much of our recent research has been focused on polynuclear ruthenium carbonyl complexes containing SnPh₃, SnPh₂ and SnPh ligands [17]. We have now investigated the reaction of the mixed metal complex HIrRu₃(CO)₁₃, **1** with HSnPh₃. We have obtained two new compounds: Ir₂Ru₂(CO)₁₁(SnPh₃)(μ-H)₃, **2** and IrRu₃(CO)₁₁(SnPh₃)₃(μ-H)₄, **3**. The major product **3** was formed by the addition of three equivalents of the Ph₃SnH to **1** in a process that resulted in an opening of the IrRu₃ cluster. The syntheses and characterizations of these new compounds are described in this report.

Experimental

General Data

Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Thermo Nicolet Avatar 360 FT-IR spectrophotometer. ¹H NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1 MHz. Mass spectrometric (MS) measurements performed by a direct-exposure probe using electron impact ionization (EI) electrospray techniques (ES) were made on a VG 70S instrument. Ru₃(CO)₁₂ and

$\text{Ir}_4(\text{CO})_{12}$ were purchased from STREM. HSnPh_3 was purchased from Aldrich and was used without further purification. $\text{HIrRu}_3(\text{CO})_{13}(\mu\text{-H})$, **1** was prepared according to a previously reported procedure [18]. Product separations were performed by TLC in air on Analtech 0.25 and 0.5 mm silica gel 60 Å F_{254} glass plates.

Reaction of $\text{HIrRu}_3(\text{CO})_{13}$ with HSnPh_3

48.89 mg (0.1394 mmol) of HSnPh_3 were added to 30.0 mg (0.0349 mmol) of $\text{HIrRu}_3(\text{CO})_{13}$ in 30 mL of hexane. The reaction solution was heated to reflux for 10 min. The color of the solution changed from red to dark brown. After cooling, the solvent was removed in vacuo, and the products were separated by TLC using a 3:1 hexane/methylene chloride solvent mixture to yield in order of elution 1.3 mg of yellow $\text{Ir}_2\text{Ru}_2(\text{CO})_{11}(\text{SnPh}_3)(\mu\text{-H})_3$, **2** (3.0% yield) and 12.1 mg of brown $\text{IrRu}_3(\text{CO})_{11}(\text{SnPh}_3)_3(\mu\text{-H})_4$, **3** (19% yield). Spectral data for **2**. IR νCO (cm^{-1} in methylene chloride): 2106(m), 2081(vs), 2074(s), 2048(m), 2037(m), 2028(m). ^1H NMR (CD_2Cl_2 , in ppm) at 25 °C: $\delta = 7.12\text{--}7.53$ (m, 15H, Ph), -18.05 (s, 1H), -19.31 (s, 2H). Mass Spec. EI/MS m/z . 1248, M^+ . Spectral data for **3**. IR νCO (cm^{-1} in hexane): 2115(vw), 2093(w), 2084(vw), 2073(w), 2051(m), 2044(vs), 2028(w), 2015(m). ^1H NMR (CD_2Cl_2 , in ppm) at 25 °C: $\delta = 7.30\text{--}7.55$ (m, 45H, Ph), $\delta = -12.09$ (s, hydride), $\delta = -15.45$ (s, hydride). Negative ion ES/MS m/z 1856, $\text{M}^+ - 2\text{H}$; 1507, $\text{M}^+ - \text{SnPh}_3$; 1479, $\text{M}^+ - \text{SnPh}_3 - \text{CO}$.

Crystallographic Analyses

Yellow single crystals of **2** suitable for X-ray diffraction analyses were obtained by slow evaporation of solvent from a hexane/methylene chloride solvent mixture at room temperature. Purple-brown single crystals of **3** suitable for X-ray diffraction analyses were obtained by slow evaporation of solvent from a hexane solvent at room temperature. Each data crystal was glued onto the end of a thin glass fiber. X-ray diffraction intensity data were measured by using a Bruker SMART APEX CCD-based diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å). The raw data frames were integrated with the SAINT + program by using a narrow-frame integration algorithm [19]. Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS [19]. Both structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on F^2 by using the SHELLXTL software package [20]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on the phenyl rings were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. Compound **2** crystallized in the triclinic crystal system. The space group P-1 was assumed and confirmed by the successful solution and refinement for the structure. Each hydride ligand was located, and refined by using geometric restraints (i.e. fixed Ir–H, Ru–H bond distances of 1.75 Å) and an isotropic thermal parameter. Compound **3** crystallized in the monoclinic system. The space group *Pn* was indicated by the systematic absences in the data and

Table 1 Crystallographic data for compounds **2** and **3**

Compound	2	3
Empirical formula	$\text{Ir}_2\text{Ru}_2\text{SnO}_{11}\text{C}_{29}\text{H}_{18}$	$\text{IrRu}_3\text{Sn}_3\text{O}_{11}\text{C}_{65}\text{H}_{49}$
Formula weight	1247.66	1857.52
Crystal system	Triclinic	Monoclinic
Lattice parameters		
<i>a</i> (Å)	8.4546(4)	9.1810(7)
<i>b</i> (Å)	9.6129(4)	20.5121(16)
<i>c</i> (Å)	22.4078(10)	17.4468(13)
α (deg)	82.499(1)	90.00
β (deg)	82.078(1)	98.839(2)
γ (deg)	68.605(1)	90.00
<i>V</i> (Å ³)	1673.10(13)	3246.6(4)
Space group	<i>P</i> -1	<i>Pn</i>
Z value	2	2
ρ_{calc} (g/cm ³)	2.477	1.900
μ (Mo K α) (mm ⁻¹)	9.599	3.911
Temperature (K)	294(2)	294(2)
$2\Theta_{\text{max}}$ (°)	52.74	53.74
No. Obs. ($I > 2\sigma(I)$)	4868	15003
No. Parameters	415	764
Goodness of fit (GOF)	1.140	1.036
Max. shift in final cycle	0.000	0.001
Residuals*: R1; wR2 ($I > 2\sigma(I)$)	0.0661; 0.1217	0.0414; 0.0972
Absorption Correction, Max/min	Multi-scan 1.000/0.772	Multi-scan 1.000/0.707
Largest peak in Final Diff. Map (e ⁻ /Å ³)	1.448	1.941

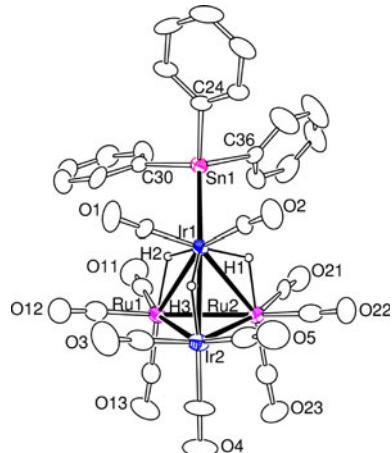
^a $R = \sum_{\text{hkl}} (|F_{\text{obs}}| - |F_{\text{calc}}|) / \sum_{\text{hkl}} |F_{\text{obs}}|$; $R_w = [\sum_{\text{hkl}} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / \sum_{\text{hkl}} w F_{\text{obs}}^2]^{1/2}$; $w = 1/\sigma^2(F_{\text{obs}})$; GOF = $[\sum_{\text{hkl}} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / (n_{\text{data}} - n_{\text{vari}})]^{1/2}$

confirmed by the successful solution and refinement for the structure. The hydride ligands were located and refined by using geometric restraints (i.e. fixed Ir–H, Ru–H bond distances of 1.75 Å) and an isotropic thermal parameter. Crystal data, data collection parameters, and results of the analyses are listed in Table 1.

Results

Two new compounds: $\text{Ir}_2\text{Ru}_2(\text{CO})_{11}(\text{SnPh}_3)(\mu\text{-H})_3$ (**2**) and $\text{IrRu}_3(\text{CO})_{11}(\text{SnPh}_3)_3(\mu\text{-H})_4$, (**3**) were obtained from the reaction of **1** with HSnPh₃ in hexane when heated to reflux for 10 min. Compound **3** is the major product, but the yield is only 19%. Compound **2** is a minor side product, 3% yield. Both compounds were characterized by a combination of IR, ¹H NMR, mass spectrum and by a single crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of

Fig. 1 An ORTEP diagram of $\text{Ir}_2\text{Ru}_2(\text{CO})_{11}(\text{SnPh}_3)(\mu\text{-H})_3$, **2** showing 30% probability thermal ellipsoids. Selected interatomic bond distances (in Å) are as follow: Ir(1)–Sn(1) = 2.6782(12), Ru(1)–Ru(2) = 2.9095(19), Ru(1)–Ir(1) = 2.8847(13), Ru(1)–Ir(2) = 2.7419(15), Ir(1)–Ru(2) = 2.9003(15), Ir(1)–Ir(2) = 2.7450(9), Ru(2)–Ir(2) = 2.7446(16)



2 is shown in Fig. 1. Compound **2** contains a tetrahedral cluster of four metal atoms: two of iridium and two of ruthenium. There are three bridging hydrido ligands. They were located and refined crystallographically by using bond distance restraints (1.75 Å). One hydrido ligand bridges the Ir–Ir bond. The other two bridge the two Ir–Ru bonds to atom Ir(1). The Ir–Ir distance, Ir(1)–Ir(2) = 2.7450(9) Å, is significantly longer than that found in $\text{Ir}_4(\text{CO})_{12}$ (2.693 Å) [21]. The Ru–Ir bonds that have bridging hydride ligands, Ru(1)–Ir(1) = 2.8847(13) Å, Ru(2)–Ir(1) = 2.9003(15) Å are significantly longer than the Ru–Ir bonds that do not have bridging hydride ligands, Ru(1)–Ir(2) = 2.7419(15) Å and Ru(2)–Ir(2) = 2.7446(16) Å. It is well-known that bridging hydride ligands increase the length of the associated metal–metal bonds [22, 23]. Similar Ru–Ir distances were observed in the iridium–ruthenium complexes $\text{IrRu}_3(\text{CO})_{11}(\text{L})(\mu\text{-H})_3$, L = PMe₃, P(OPh)₃ and AsPh₃ [24]. The Ru–Ru bond distance Ru(1)–Ru(2) = 2.9095(19) Å is slightly longer than those in $\text{Ru}_3(\text{CO})_{12}$ (ave 2.854(1) Å) [25]. The 1H NMR spectrum of **2** exhibits two high resonances at –18.05 (1H) and –19.31 (2H) ppm for the hydride ligands. Compound **2** contains one SnPh₃ ligand that is coordinated to the iridium atom, Ir(1). The Ir–Sn distance, Ir(1)–Sn(1) = 2.6782(12) Å, is similar to the Ir–Sn distances to the three SnPh₃ ligands found in the tri-iridium cluster complex $\text{Ir}_3(\text{CO})_6(\mu\text{-SnPh}_2)_3(\text{SnPh}_3)_3$: 2.6736(9) Å, 2.6981(11) Å and 2.6888(10) Å [15]. There are 11 linear terminal carbonyl ligands distributed among the metal atoms as shown in Fig. 1. Overall, the cluster contains a total of 60 valence electrons which is exactly the number required for a tetrahedral cluster complex in which each of the metal atoms obeys the 18 electron rule.

An ORTEP diagram of the molecular structure of **3** is shown in Fig. 2. Compound **3** consists of an open “butterfly” cluster of four metal atoms consisting one iridium and three ruthenium atoms. The cluster is nearly planar; the dihedral angle between the planes Ru(1)–Ru(2)–Ir(1) and Ru(2)–Ru(3)–Ir(1) is 179.3°. There are four bridging hydride ligands that go around the periphery of the cluster. The hydride-bridged Ir–Ru bond distances, Ir(1)–Ru(1) = 2.9695(9) Å and Ir(1)–Ru(3) = 2.9684(9) Å, are

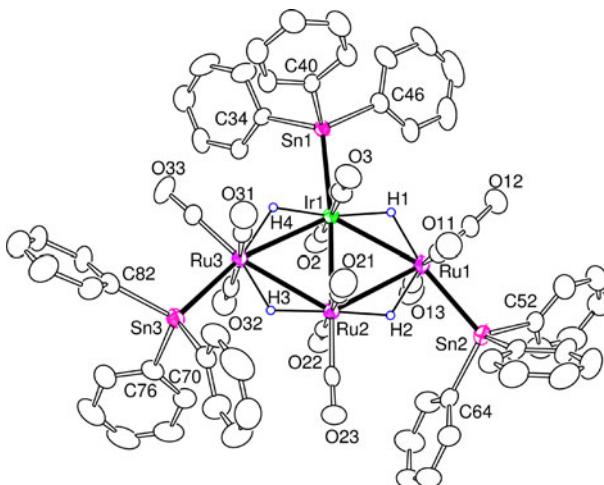
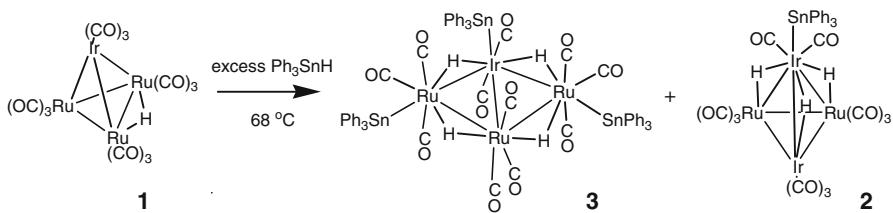


Fig. 2 An ORTEP diagram of $\text{IrRu}_3(\text{CO})_{11}(\text{SnPh}_3)_4(\mu\text{-H})_4$, **3** showing 30% probability thermal ellipsoids. Selected bond distances (in Å) are as follow: Ir(1)–Ru(1) = 2.9695(9), Ir(1)–Ru(2) = 2.8489(6), Ir(1)–Ru(3) = 2.9684(9), Ru(1)–Ru(2) = 3.0283(12), Ru(2)–Ru(3) = 3.0275(11), Ir(1)–Sn(1) = 2.6588(6), Ru(1)–Sn(2) = 2.6851(11), Ru(3)–Sn(3) = 2.6835(11)

significantly longer than hydride-bridged Ir–Ru bonds observed in **2**, and are much longer than the nonhydride bridged Ir–Ru bond, Ir(1)–Ru(2) = 2.8489(6) Å, that forms the hinge of the butterfly. The latter is also much longer than the non-hydride bridged Ru–Ir bonds in **2**. The hydride-bridged Ru–Ru bonds are the longest in the molecule, Ru(1)–Ru(2) = 3.0283(12) Å, Ru(2)–Ru(3) = 3.0275(11) Å. This is due first to the bond lengthening effects of the hydride ligands [22, 23], but may also be due in part to steric crowding effects that result from the presence of three SnPh_3 ligands. According to symmetry, the hydride ligands are exist in two equivalent pairs, those that bridge Ir–Ru bonds and those that bridge Ru–Ru bonds. Appropriately, the ^1H NMR spectrum of **3** exhibits two high-field singlets at $\delta = -12.09$ and -15.45 in a 2:2 ratio. The tin atoms of all three SnPh_3 ligands lie essentially in the plane of the cluster. There is one SnPh_3 ligand on the iridium atom and one on each of the ruthenium atoms on the “wing-tip” of the butterfly. The Ir–Sn distance, Ir(1)–Sn(1) = 2.6588(6) Å, is similar to that in **2**. The Ru–Sn distances are slightly longer than the Ir–Sn distance, Ru(1)–Sn(2) = 2.6851(11) Å and Ru(3)–Sn(3) = 2.6835(11) Å, but are similar to the Ru–Sn distances observed in a number of triruthenium complexes containing SnPh_3 ligands that have been characterized recently, e.g. $\text{Ru}_3(\text{CO})_9(\text{SnPh}_3)_2(\text{NCMe})(\mu\text{-H})_2$: Ru(1)–Sn(1) = 2.6773(6), Ru(2)–Sn(2) = 2.6488(6), Ru(4)–Sn(3) = 2.6799(6), Ru(5)–Sn(4) = 2.6553(6) [14]; $\text{Ru}_3(\text{CO})_{10}(\text{SnPh}_3)_2(\mu\text{-H})_2$: Ru(1)–Sn(1) = 2.6891(7), Ru(2)–Sn(2) = 2.6565(7) [14]; $\text{Ru}_3(\text{CO})_7(\text{SnPh}_3)_3(\text{NCMe})_2(\mu\text{-H})_3$: Ru(1)–Sn(1) = 2.6610(6), Ru(2)–Sn(2) = 2.6681(6), Ru(3)–Sn(3) = 2.6745(6) [14]; $\text{Ru}_3(\text{CO})_9(\text{SnPh}_3)_3(\mu\text{-H})_3$: Ru(2)–Sn(2) = 2.6892(7) [14]. The cluster contains a total of 62 valence electrons which is consistent with a four metal cluster having five metal–metal bonds as found in **3**.

**Scheme 3**

Discussion

A summary of the reactions described in this report is shown in the Scheme 3. Two new iridium–ruthenium cluster compounds **2** and **3** containing SnPh_3 ligands were obtained by the reaction of **1** with HSnPh_3 . Compound **2** contains two iridium atoms and must have been formed by an unobserved metal–metal exchange process of some sort because the reagent **1** contains only one iridium atom. Compound **2** contains one SnPh_3 ligand that is coordinated to one of the iridium atoms. The major product **3** was formed as a result of the addition of three equivalents of HSnPh_3 to **1** and the elimination of two CO ligands. In order to accommodate the net increase in ligands and the increase in electrons on the metal atoms of the cluster, the metal cluster has opened to form a butterfly cluster with five metal–metal bonds that is nearly planar.

As we have recently shown for a number of related compounds, it is anticipated that these new trimetallic complexes will also serve as precursors to new nanoscale heterogeneous particles [26] and hydrogenation catalysts [10–13] when deposited and activated on suitable supports.

Supplementary Material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC 768178 for compound **2**, CCDC 768179 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK [Fax. (int code) +44(1223)336-033, or Email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>.

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