

A New Method for Introducing Tin Ligands into Tetrairidium Dodecacarbonyl

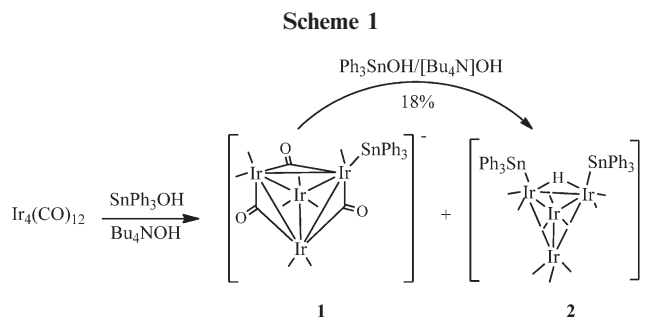
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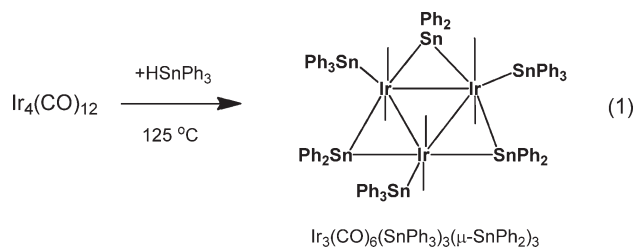
Received December 29, 2010

Summary: The reaction of Ph_3SnOH with $\text{Ir}_4(\text{CO})_{12}$ in the presence of $[\text{Bu}_4\text{N}]\text{OH}$ in methanol solvent gave two products, $[\text{Bu}_4\text{N}][\text{Ir}_4(\text{CO})_{11}(\text{SnPh}_3)]$ (**1**; 45% yield) and $[\text{Bu}_4\text{N}][\text{Ir}_4(\text{CO})_{10}(\text{SnPh}_3)_2(\mu\text{-H})]$ (**2**; 5.5% yield), and the reaction of $\text{Ir}_4(\text{CO})_{11}(\text{PPh}_3)$ with Ph_3SnOH in the presence of $[\text{Bu}_4\text{N}]\text{OH}$ gave the complex $\text{Ir}_4(\text{CO})_{10}(\text{SnPh}_3)(\text{PPh}_3)(\mu\text{-H})$ (**3**) in 44% yield. It is proposed that the reactions occur by the addition of the anion $[\text{OSnPh}_3]^-$ generated in situ to a CO ligand of the $\text{Ir}_4(\text{CO})_{12}$ to form a stannyl-substituted metallocarboxylate ligand that subsequently loses CO_2 and transfers the SnPh_3 group to a metal atom.

It has been known for many years that tin is an important modifier for both homogeneous¹ and heterogeneous^{2–4} transition-metal catalysts. Tin has been shown to improve the selectivity of certain types of catalytic hydrogenation reactions.^{5–9} When it is combined with platinum, it can even increase catalytic activity.^{3,4} Recent studies have shown that supported multimetallic nanocluster catalysts can be prepared with almost stoichiometric precision when they are created by using multimetallic cluster complexes as catalyst precursors.^{5–9} Iridium is known to exhibit interesting catalytic properties;¹⁰ however, due to its low reactivity it is difficult to introduce tin ligands in tetrairidium dodecacarbonyl. Some tin-substituted



tetrairidium complexes have been obtained from the more reactive anion $[\text{Ir}_4(\text{CO})_{11}\text{Br}]^-$.^{11,12} We have recently shown that the triiridium complex $\text{Ir}_3(\text{CO})_6(\mu\text{-SnPh}_2)_3(\text{SnPh}_3)_3$ is formed in low yield from the reaction of $\text{Ir}_4(\text{CO})_{12}$ with H_2SnPh_3 at 125 °C (eq 1), but this reaction leads to degradation of the tetrairidium cluster.¹³ In an effort to find a more convenient route to tetrairidium–tin carbonyl complexes, we have examined the reactions of $\text{Ir}_4(\text{CO})_{12}$ and $\text{Ir}_4(\text{CO})_{11}(\text{PPh}_3)$ with Ph_3SnOH under basic conditions.



The two products $[\text{Bu}_4\text{N}][\text{Ir}_4(\text{CO})_{11}(\text{SnPh}_3)]$ (**1**; 45% yield) and $[\text{Bu}_4\text{N}][\text{Ir}_4(\text{CO})_{10}(\text{SnPh}_3)_2(\mu\text{-H})]$ (**2**; 5.5% yield) were obtained from the reaction of $\text{Ir}_4(\text{CO})_{12}$ with an excess of Ph_3SnOH in the presence of $[\text{Bu}_4\text{N}]\text{OH}$ in methanol solvent at reflux for 30 min (see Scheme 1). Note that these products are not obtained in the absence of base.

Compound **2** can be obtained from **1** in 18% yield by treatment with an excess of Ph_3SnOH in methanol solvent in the presence of $[\text{Bu}_4\text{N}]\text{OH}$ at 25 °C over 15 h. The structures of the complex anions of **1** and **2** were established by a combination of IR, ^1H NMR, negative ion mass spectra, and single-crystal X-ray diffraction analyses of their $[\text{Et}_4\text{N}]^+$ and $[\text{Bu}_4\text{N}]^+$ salts, respectively. An ORTEP diagram of the structure of the anion of **1** is shown in Figure 1. The anion consists of a tetrahedral cluster of four iridium atoms with 1 SnPh_3 ligand and 11 carbonyl ligands. Three of the carbonyl

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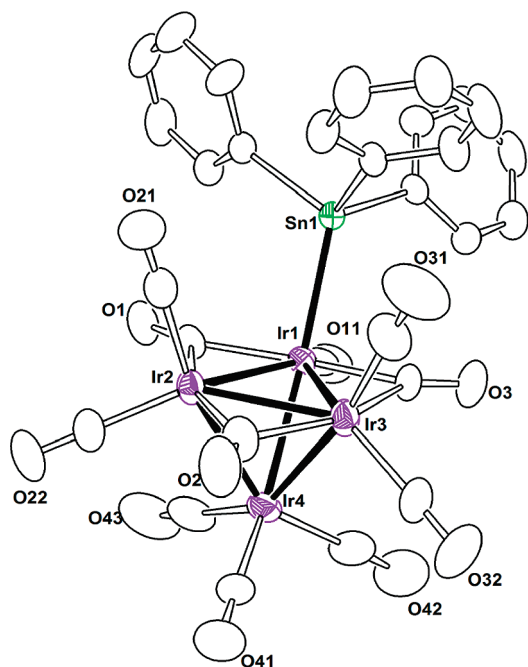


Figure 1. ORTEP diagram of the molecular structure of the anion $[\text{Ir}_4(\text{CO})_{11}(\text{SnPh}_3)]^-$ of **1-Et**, showing 30% probability thermal ellipsoids. The hydrogen atoms on the phenyl rings are omitted for clarity. Selected interatomic bond distances (Å) and angles (deg) of compound **1**: Ir1–Ir2 = 2.7610(3), Ir1–Ir3 = 2.7616(4), Ir1–Ir4 = 2.7435(4), Ir2–Ir3 = 2.7061(4), Ir2–Ir4 = 2.7210(4), Ir3–Ir4 = 2.7240(4), Ir1–Sn1 = 2.6358(4); Sn1–Ir1–Ir2 = 107.660(13), Ir4–Ir1–Sn1 = 164.246(15).

ligands are edge-bridging ligands about the Ir(1)–Ir(2)–Ir(3) triangular group of metal atoms. All the others are linear terminal carbonyl ligands. The Ir–Ir bond distances range from 2.7061(4) to 2.7610(3) Å. These values are slightly longer than the Ir–Ir distances of 2.692 Å found in $\text{Ir}_4(\text{CO})_{12}$, which has a disordered structure in the solid state.¹⁴ The SnPh_3 ligand lies approximately trans to the Ir1–Ir4 bond: Ir4–Ir1–Sn1 = 164.246(15)°. The Ir1–Sn1 distance, 2.6358(4) Å, is significantly shorter than the Ir–Sn distances to the SnPh_3 ligands found in the crowded triiridium cluster complex $\text{Ir}_3(\text{CO})_6(\text{SnPh}_3)_3(\mu\text{-SnPh}_2)_3$ (2.6736(9)–2.6981(11) Å),¹³ but it is similar to the Ir–Sn distance of 2.6216(5) Å found in the less crowded monoiridium complex $\text{Ir}(\text{COD})(\text{CO})_2\text{SnPh}_3$.¹⁵

An ORTEP diagram of the structure of the anion of **2** is shown in Figure 2. The anion consists of a tetrahedral cluster of four iridium atoms with two SnPh_3 ligands on different iridium atoms, Ir(1) and Ir(2). Each tin-substituted iridium atom contains two linear terminal carbonyl ligands; the other two iridium atoms have three carbonyl ligands. There is a bridging hydrido ligand across the Ir(1)–Ir(2) bond: $\delta -19.69$ ($^2J_{\text{Sn-H}} = 9.51$ Hz) in the H NMR spectrum. As expected,¹⁶ the hydride-bridged Ir–Ir distance, 2.8609(6) Å, is significantly longer than the unbridged Ir–Ir distances, which range from 2.7074(7) to 2.7225(7) Å. The Ir–Sn bond distances, Ir1–Sn1 = 2.6449(9) Å and Ir2–Sn2 = 2.6625(10) Å, are similar to those found in **1**. Each of the metal atoms in **1** and **2** has an 18-electron configuration.

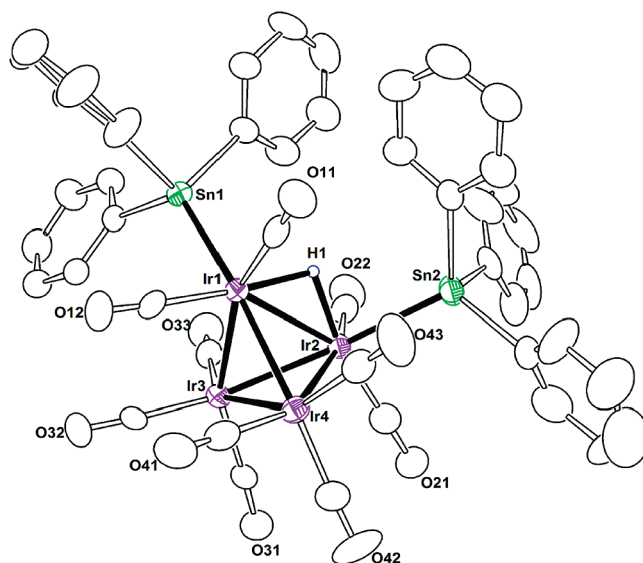


Figure 2. ORTEP diagram of the molecular structure of $[\text{H}\text{Ir}_4(\text{CO})_{10}(\text{SnPh}_3)_2]^-$ (**2**), showing 30% probability thermal ellipsoids. The hydrogen atoms on the phenyl rings are omitted for clarity. Selected interatomic bond distances (Å) and angles (deg): Ir1–Ir3 = 2.7122(6), Ir1–Ir4 = 2.7184(6), Ir1–Ir2 = 2.8608(6), Ir2–Ir4 = 2.7074(7), Ir2–Ir3 = 2.7225(7), Ir1–H1 = 1.75(2), Ir1–Sn1 = 2.6449(9), Ir2–Sn2 = 2.6626(10), Ir2–H1 = 1.74(2), Ir3–Ir4 = 2.7206(7); Sn1–Ir1–Ir4 = 165.75(3), Sn2–Ir2–Ir3 = 163.86(3).

For comparison, we have also investigated the reaction of the PPh_3 derivative of $\text{Ir}_4(\text{CO})_{11}(\text{PPh}_3)$ ¹⁷ with Ph_3SnOH . The new tin complex $\text{Ir}_4(\text{CO})_{10}(\text{SnPh}_3)(\text{PPh}_3)(\mu\text{-H})$ (**3**) was isolated by TLC in 44% yield after stirring a solution of an excess of Ph_3SnOH with $\text{Ir}_4(\text{CO})_{11}(\text{PPh}_3)$ and $[\text{Bu}_4\text{N}]\text{OH}$ for 16 h at 25 °C. An ORTEP diagram of the molecular structure of **3** is shown in Figure 3. In the solid state, there are two independent molecules of **3** in the asymmetric crystal unit. Both molecules are structurally similar and contain one PPh_3 ligand and one SnPh_3 ligand. The PPh_3 and SnPh_3 ligands are disordered in both molecules; thus, the Ir–Sn/P distances measured here are not of high accuracy, but the structural analysis does confirm the gross structure of the molecule. The tetrahedral arrangement of iridium atoms is not disordered; therefore, the Ir–Ir distances are reliable. The Ir–Ir bond between the PPh_3 and SnPh_3 ligands contains a bridging hydrido ligand and this Ir–Ir distance, Ir1–Ir2 = 2.8851(5) Å for molecule 1 and Ir5–Ir6 = 2.8730(5) Å for molecule 2, is significantly longer than the other Ir–Ir distances, which range from 2.7012(5) to 2.7159(5) Å.¹⁶ The hydride ligand exhibits the usual upfield shift: $\delta -18.37$. The phosphine ligand exhibits a typical ^{31}P resonance shift: $\delta -15.18$ ppm.

Although **3** is an uncharged, neutral molecule, we have not yet been able to isolate any uncharged forms of the two anions of **1** and **2** by acidification with protic acids. This may simply be due to the relative differences in basicity of the corresponding anions. Because of the presence of the PPh_3 ligand, a deprotonated form of **3** would be considerably more basic than that of **1** and thus would be more stable in its protonated form. These studies are still in progress.

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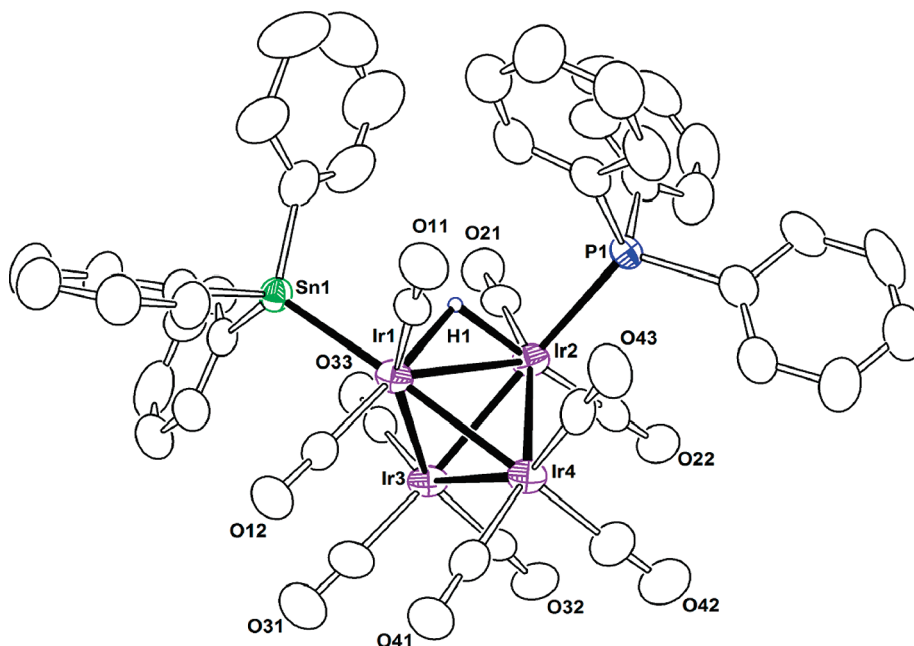
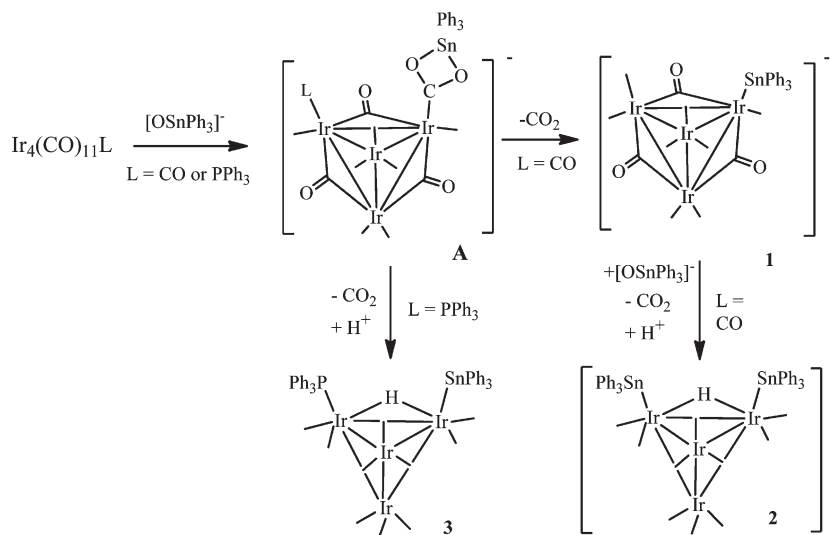


Figure 3. ORTEP diagram of the molecular structure of $\text{HIr}_4(\text{CO})_{10}(\text{SnPh}_3)(\text{PPh}_3)$ (**3**), showing 30% probability thermal ellipsoids (the disorder between Sn and P is not shown). The hydrogen atoms on the phenyl rings are omitted for clarity. Selected interatomic bond distances (Å) and angles (deg): molecule 1, $\text{Ir1}-\text{Ir2} = 2.8851(5)$, $\text{Ir2}-\text{Ir3} = 2.7095(5)$, $\text{Ir2}-\text{Ir4} = 2.7135(5)$, $\text{Ir1}-\text{Sn1}(\text{P2}) = 2.5212(10)$, $\text{Ir1}-\text{Ir3} = 2.7100(5)$, $\text{Ir1}-\text{Ir4} = 2.7142(5)$, $\text{Ir3}-\text{Ir4} = 2.7012(5)$, $\text{Ir1}-\text{H1} = 1.76(5)$, $\text{Ir2}-\text{P1}(\text{Sn2}) = 2.5126(10)$, $\text{Ir2}-\text{H1} = 1.79(6)$, $\text{Sn1}(\text{P1})-\text{Ir1}-\text{Ir2} = 113.17(3)$, $\text{P1}(\text{Sn2})-\text{Ir2}-\text{Ir1} = 112.69(3)$; molecule 2, $\text{Ir5}-\text{Ir6} = 2.8730(5)$, $\text{Ir5}-\text{Ir7} = 2.7149(6)$, $\text{Ir5}-\text{Ir8} = 2.7159(5)$, $\text{Ir6}-\text{Ir7} = 2.7054(5)$, $\text{Ir6}-\text{Ir8} = 2.7109(5)$, $\text{Ir7}-\text{Ir8} = 2.7058(6)$, $\text{Ir5}-\text{H2} = 1.78(7)$, $\text{Ir5}-\text{P3}(\text{Sn4}) = 2.4491(14)$, $\text{Ir6}-\text{Sn3}(\text{P4}) = 2.6079(9)$, $\text{Ir6}-\text{H2} = 1.78(7)$, $\text{Sn3}(\text{P4})-\text{Ir6}-\text{Ir5} = 113.14(2)$, $\text{P3}(\text{Sn4})-\text{Ir5}-\text{Ir6} = 109.39(3)$.

Scheme 2



It is worthwhile to consider possible mechanisms for the formation of the anions **1** and **2** and the neutral molecule **3**. A number of years ago, Garlaschelli et al. showed that alkoxides add to the carbonyl ligands of $\text{Ir}_4(\text{CO})_{12}$ to form metallocarboxylate ligands.¹⁸ For the basic media used herein, it is proposed that a similar process involving $[\text{OSnPh}_3]^-$, generated in situ, could lead to a similar triphenylstannyl-substituted metallocarboxylate, such as **A** (see Scheme 2). Stannyl-substituted metallocarboxylate complexes have

been observed previously, although they have been obtained by different procedures.^{19–21} In those complexes, the tin atom is typically bonded to both oxygen atoms of the carboxylate group, but even so these ligand groups are known to

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undergo decarboxylations that lead to the formation of metal–tin bonds.¹⁹ A similar loss of CO₂ from **A** and a transfer of the SnPh₃ group to an iridium atom should lead to the anion **1**. A second application of this process to **1** with a subsequent proton addition would lead to **2**, and a similar process occurring with Ir₄(CO)₁₁(PPh₃) would yield **3**.

It has not yet been possible to synthesize the compounds **1–3** by other methods. We believe that reactions of [OSnR₃][−] anions with metal carbonyl complexes could be general and lead to a variety of new tin-containing transition-metal carbonyl complexes that may be useful as precursors to new tin-containing homogeneous and heterogeneous transition-metal catalysts. Further studies of the reactions of Ph₃SnOH

with transition-metal carbonyl complexes in basic media are in progress.

Acknowledgment. This research was supported by the National Science Foundation under Grant No. CHE-0743190. We thank the USC NanoCenter for partial support of this work.

Supporting Information Available: Text, a table, figures, and CIF files giving details for the synthesis of compounds **1–3** and crystal data for the structural analyses of compounds **1-Et**, **2**, and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.