# A New Method for Introducing Tin Ligands into Tetrairidium Dodecacarbonyl 

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Summary: The reaction of $\mathrm{Ph}_{3} \mathrm{SnOH}$ with $\mathrm{Ir}_{4}(\mathrm{CO})_{12}$ in the presence of $\left[\mathrm{Bu} u_{4} \mathrm{~N}\right] \mathrm{OH}$ in methanol solvent gave two products, $\left[B u_{4} N\right]\left[I_{4}(\mathrm{CO})_{I l}\left(\mathrm{SnPh}_{3}\right)\right](1 ; 45 \%$ yield $)$ and $\left[B u_{4} N\right]\left[\mathrm{Ir}_{4^{-}}\right.$ $\left.(\mathrm{CO})_{10}\left(\mathrm{SnPh}_{3}\right)_{2}(\mu-H)\right](2 ; 5.5 \%$ yield $)$, and the reaction of $\mathrm{Ir}_{4}(\mathrm{CO})_{1 l}\left(\mathrm{PPh}_{3}\right)$ with $\mathrm{Ph}_{3} \mathrm{SnOH}$ in the presence of $\left[\mathrm{Bu}{ }_{4} \mathrm{~N}\right] \mathrm{OH}$ gave the complex $\mathrm{Ir}_{4}\left(\mathrm{CO}_{10}\left(\mathrm{SnPh}_{3}\right)\left(\mathrm{PPh}_{3}\right)(\mu-H)(3)\right.$ in $44 \%$ yield. It is proposed that the reactions occur by the addition of the anion $\left[\mathrm{OSnPh}_{3}\right]^{-}$generated in situ to a CO ligand of the $\mathrm{Ir}_{4}(\mathrm{CO})_{12}$ to form a stannyl-substituted metallocarboxylate ligand that subsequently loses $\mathrm{CO}_{2}$ and transfers the $\mathrm{SnPh}_{3}$ group to a metal atom.

It has been known for many years that tin is an important modifier for both homogeneous ${ }^{1}$ 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 in introduce tin ligands in tetrairidium dodecacarbonyl. Some tin-substituted

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tetrairidium complexes have been obtained from the more reactive anion $\left[\mathrm{Ir}_{4}(\mathrm{CO})_{11} \mathrm{Br}\right]^{-} .{ }^{11,12}$ We have recently shown that the triiridum complex $\mathrm{Ir}_{3}(\mathrm{CO})_{6}\left(u-\mathrm{SnPh}_{2}\right)_{3}\left(\mathrm{SnPh}_{3}\right)_{3}$ is formed in low yield from the reaction of $\mathrm{Ir}_{4}(\mathrm{CO})_{12}$ with $\mathrm{HSnPh}_{3}$ at $125^{\circ} \mathrm{C}$ (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 $\mathrm{Ir}_{4}(\mathrm{CO})_{12}$ and $\mathrm{Ir}_{4}(\mathrm{CO})_{11}\left(\mathrm{PPh}_{3}\right)$ with $\mathrm{Ph}_{3} \mathrm{SnOH}$ under basic conditions.


The two products $\left[\mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{Ir}_{4}(\mathrm{CO})_{11}\left(\mathrm{SnPh}_{3}\right)\right](\mathbf{1} ; 45 \%$ yield $)$ and $\left[\mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{Ir}_{4}(\mathrm{CO})_{10}\left(\mathrm{SnPh}_{3}\right)_{2}(\mu-\mathrm{H})\right](2 ; 5.5 \%$ yield) were obtained from the reaction of $\mathrm{Ir}_{4}(\mathrm{CO})_{12}$ with an excess of $\mathrm{Ph}_{3} \mathrm{SnOH}$ in the presence of $\left[\mathrm{Bu}_{4} \mathrm{~N}\right] \mathrm{OH}$ 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 $\mathrm{Ph}_{3} \mathrm{SnOH}$ in methanol solvent in the presence of $\left[\mathrm{Bu}_{4} \mathrm{~N}\right] \mathrm{OH}$ at $25^{\circ} \mathrm{C}$ over 15 h . The structures of the complex anions of $\mathbf{1}$ and $\mathbf{2}$ were established by a combination of IR, ${ }^{1} \mathrm{H}$ NMR, negative ion mass spectra, and single-crystal X-ray diffraction analyses of their $\left[\mathrm{Et}_{4} \mathrm{~N}\right]^{+}$and $\left[\mathrm{Bu}_{4} \mathrm{~N}\right]^{+}$salts, respectively. An ORTEP diagram of the structure of the anion of $\mathbf{1}$ is shown in Figure 1. The anion consists of a tetrahedral cluster of four iridium atoms with 1 $\mathrm{SnPh}_{3}$ ligand and 11 carbonyl ligands. Three of the carbonyl

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Figure 1. ORTEP diagram of the molecular structure of the anion $\left[\mathrm{Ir}_{4}(\mathrm{CO})_{11}\left(\mathrm{SnPh}_{3}\right)\right]^{-}$of $\mathbf{1 - E t}$, showing $30 \%$ probability thermal ellipsoids. The hydrogen atoms on the phenyl rings are omitted for clarity. Selected interatomic bond distances $(\AA)$ and angles (deg) of compound 1: Ir1-Ir2 = 2.7610(3), $\operatorname{Ir} 1-\operatorname{Ir} 3=$ $2.7616(4), \operatorname{Ir} 1-\operatorname{Ir} 4=2.7435(4), \operatorname{Ir} 2-\operatorname{Ir} 3=2.7061(4), \operatorname{Ir} 2-\operatorname{Ir} 4=$ $2.7210(4), \operatorname{Ir} 3-\operatorname{Ir} 4=2.7240(4), \operatorname{Ir} 1-\operatorname{Sn} 1=2.6358(4) ; \operatorname{Sn} 1-\operatorname{Ir} 1-$ $\operatorname{Ir} 2=107.660(13), \operatorname{Ir} 4-\operatorname{Ir} 1-\operatorname{Sn} 1=164.246(15)$.
ligands are edge-bridging ligands about the $\operatorname{Ir}(1)-\operatorname{Ir}(2)-\operatorname{Ir}-$ (3) triangular group of metal atoms. All the others are linear terminal carbonyl ligands. The $\mathrm{Ir}-\mathrm{Ir}$ bond distances range from $2.7061(4)$ to $2.7610(3) \AA$. These values are slightly longer than the $\mathrm{Ir}-\mathrm{Ir}$ distances of $2.692 \AA$ found in $\mathrm{Ir}_{4}$ $(\mathrm{CO})_{12}$, which has a disordered structure in the solid state. ${ }^{14}$ The $\mathrm{SnPh}_{3}$ ligand lies approximately trans to the Ir1-Ir4 bond: $\operatorname{Ir} 4-\operatorname{Ir} 1-\operatorname{Sn} 1=164.246(15)^{\circ}$. The $\operatorname{Ir} 1-\operatorname{Sn} 1$ distance, 2.6358(4) $\AA$, is significantly shorter than the $\mathrm{Ir}-\mathrm{Sn}$ distances to the $\mathrm{SnPh}_{3}$ ligands found in the crowded triiridium cluster complex $\mathrm{Ir}_{3}(\mathrm{CO})_{6}\left(\mathrm{SnPh}_{3}\right)_{3}\left(u-\mathrm{SnPh}_{2}\right)_{3}(2.6736(9)-2.6981(11) \AA),{ }^{13}$ but it is similar to the $\mathrm{Ir}-\mathrm{Sn}$ distance of $2.6216(5) \AA$ found in the less crowded monoiridium complex $\operatorname{Ir}(\mathrm{COD})(\mathrm{CO})_{2} \mathrm{SnPh}_{3} .{ }^{15}$

An ORTEP diagram of the structure of the anion of $\mathbf{2}$ is shown in Figure 2. The anion consists of a tetrahedral cluster of four iridium atoms with two $\mathrm{SnPh}_{3}$ ligands on different iridium atoms, $\operatorname{Ir}(1)$ and $\operatorname{Ir}(2)$. 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 $\operatorname{Ir}(1)-\operatorname{Ir}(2)$ bond: $\delta-19.69\left({ }^{2} J_{\mathrm{Sn}-\mathrm{H}}=9.51 \mathrm{~Hz}\right)$ in the H NMR spectrum. As expected, ${ }^{16}$ the hydride-bridged $\mathrm{Ir}-\mathrm{Ir}$ distance, $2.8609(6) \AA$, is significantly longer than the unbridged $\mathrm{Ir}-\mathrm{Ir}$ distances, which range from $2.7074(7)$ to $2.7225(7) \AA$. The $\mathrm{Ir}-\mathrm{Sn}$ bond distances, $\operatorname{Ir} 1-\operatorname{Sn} 1=2.6449(9) \AA$ and $\operatorname{Ir} 2-\operatorname{Sn} 2=$ $2.6625(10) \AA$, are similar to those found in $\mathbf{1}$. Each of the metal atoms in $\mathbf{1}$ and $\mathbf{2}$ has an 18-electron configuration.

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Figure 2. ORTEP diagram of the molecular structure of $\left[\mathrm{HIr}_{4}(\mathrm{CO})_{10}\left(\mathrm{SnPh}_{3}\right)_{2}\right]^{-}$(2), showing $30 \%$ probability thermal ellipsoids. The hydrogen atoms on the phenyl rings are omitted for clarity. Selected interatomic bond distances ( $\AA$ ) and angles (deg): $\operatorname{Ir} 1-\operatorname{Ir} 3=2.7122(6), \operatorname{Ir} 1-\operatorname{Ir} 4=2.7184(6), \operatorname{Ir} 1-\operatorname{Ir} 2=$ 2.8608(6), Ir2-Ir4 = 2.7074(7), Ir2-Ir3 = 2.7225(7), $\operatorname{Ir} 1-$ $\mathrm{H} 1=1.75(2), \operatorname{Ir} 1-\mathrm{Sn} 1=2.6449(9), \operatorname{Ir} 2-\mathrm{Sn} 2=2.6626(10)$, 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 $\mathrm{PPh}_{3}$ derivative of $\mathrm{Ir}_{4}(\mathrm{CO})_{11}\left(\mathrm{PPh}_{3}\right)^{17}$ with $\mathrm{Ph}_{3} \mathrm{SnOH}$. The new tin complex $\mathrm{Ir}_{4}(\mathrm{CO})_{10}\left(\mathrm{SnPh}_{3}\right)\left(\mathrm{PPh}_{3}\right)(\mu-\mathrm{H})(3)$ was isolated by TLC in $44 \%$ yield after stirring a solution of an excess of $\mathrm{Ph}_{3} \mathrm{SnOH}$ with $\mathrm{Ir}_{4}(\mathrm{CO})_{11}\left(\mathrm{PPh}_{3}\right)$ and $\left[\mathrm{Bu}_{4} \mathrm{~N}\right] \mathrm{OH}$ for 16 h at $25^{\circ} \mathrm{C}$. An ORTEP diagram of the molecular structure of $\mathbf{3}$ is shown in Figure 3. In the solid state, there are two independent molecules of $\mathbf{3}$ in the asymmetric crystal unit. Both molecules are structurally similar and contain one $\mathrm{PPh}_{3}$ ligand and one $\mathrm{SnPh}_{3}$ ligand. The $\mathrm{PPh}_{3}$ and $\mathrm{SnPh}_{3}$ ligands are disordered in both molecules; thus, the $\mathrm{Ir}-\mathrm{Sn} / \mathrm{P}$ 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 $\mathrm{Ir}-\mathrm{Ir}$ distances are reliable. $\mathrm{The} \mathrm{Ir}-\mathrm{Ir}$ bond between the $\mathrm{PPh}_{3}$ and $\mathrm{SnPh}_{3}$ ligands contains a bridging hydrido ligand and this $\mathrm{Ir}-\mathrm{Ir}$ distance, $\mathrm{Ir} 1-\mathrm{Ir} 2=$ 2.8851(5) $\AA$ for molecule 1 and $\operatorname{Ir} 5-\operatorname{Ir} 6=2.8730(5) ~ \AA$ for molecule 2, is significantly longer than the other $\mathrm{Ir}-\mathrm{Ir}$ distances, which range from $2.7012(5)$ to $2.7159(5) \AA .{ }^{16}$ The hydride ligand exhibits the usual upfield shift: $\delta-18.37$. The phosphine ligand exhibits a typical ${ }^{31} \mathrm{P}$ resonance shift: $\delta-15.18 \mathrm{ppm}$.

Although $\mathbf{3}$ is an uncharged, neutral molecule, we have not yet been able to isolate any uncharged forms of the two anions of $\mathbf{1}$ and $\mathbf{2}$ 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 $\mathrm{PPh}_{3}$ ligand, a deprotonated form of $\mathbf{3}$ would be considerably more basic than that of $\mathbf{1}$ 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 $\mathrm{HIr}_{4}(\mathrm{CO})_{10}\left(\mathrm{SnPh}_{3}\right)\left(\mathrm{PPh}_{3}\right)(3)$, 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 $(\mathrm{A})$ and angles (deg): molecule $1, \operatorname{Ir} 1-\operatorname{Ir} 2=2.8851(5), \operatorname{Ir} 2-\operatorname{Ir} 32.7095(5), \operatorname{Ir} 2-\operatorname{Ir} 4=2.7135(5), \operatorname{Ir} 1-\operatorname{Sn} 1(\mathrm{P} 2)=$ $2.5212(10), \operatorname{Ir} 1-\operatorname{Ir} 3=2.7100(5), \operatorname{Ir} 1-\operatorname{Ir} 4=2.7142(5), \operatorname{Ir} 3-\operatorname{Ir} 4=2.7012(5), \operatorname{Ir} 1-H 1=1.76(5), \operatorname{Ir} 2-\mathrm{P} 1(\operatorname{Sn} 2)=2.5126(10), \operatorname{Ir} 2-$ $\mathrm{H} 1=1.79(6), \mathrm{Sn} 1(\mathrm{P} 1)-\operatorname{Ir} 1-\operatorname{Ir} 2=113.17(3), \mathrm{P} 1(\mathrm{Sn} 2)-\operatorname{Ir} 2-\operatorname{Ir} 1=112.69(3) ;$ molecule $2, \operatorname{Ir} 5-\operatorname{Ir} 6=2.8730(5), \operatorname{Ir} 5-\operatorname{Ir} 7=2.7149(6)$, $\operatorname{Ir} 5-\operatorname{Ir} 8=2.7159(5), \operatorname{Ir} 6-\operatorname{Ir} 7=2.7054(5), \operatorname{Ir} 6-\operatorname{Ir} 8=2.7109(5), \operatorname{Ir} 7-\operatorname{Ir} 8=2.7058(6), \operatorname{Ir} 5-H 2=1.78(7), \operatorname{Ir} 5-\mathrm{P} 3(\operatorname{Sn} 4)=2.4491(14)$, $\operatorname{Ir} 6-\operatorname{Sn} 3(P 4)=2.6079(9), \operatorname{Ir} 6-\mathrm{H} 2=1.78(7), \operatorname{Sn} 3(\mathrm{P} 4)-\operatorname{Ir} 6-\operatorname{Ir} 5=113.14(2), \mathrm{P} 3(\operatorname{Sn} 4)-\operatorname{Ir} 5-\operatorname{Ir} 6=109.39(3)$.

Scheme 2


It is worthwhile to consider possible mechanisms for the formation of the anions $\mathbf{1}$ and $\mathbf{2}$ and the neutral molecule 3. A number of years ago, Garlaschelli et al. showed that alkoxides add to the carbonyl ligands of $\mathrm{Ir}_{4}(\mathrm{CO})_{12}$ to form metallocarboxylate ligands. ${ }^{18}$ For the basic media used herein, it is proposed that a similar process involving $\left[\mathrm{OSnPh}_{3}\right]^{-}$, generated in situ, could lead to a similar triphenylstannylsubstituted metallocarboxylate, such as A (see Scheme 2). Stannyl-substituted metallocarboxylate complexes have

[^4]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

[^5]undergo decarboxylations that lead to the formation of metal-tin bonds. ${ }^{19}$ A similar loss of $\mathrm{CO}_{2}$ from $\mathbf{A}$ and a transfer of the $\mathrm{SnPh}_{3}$ 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 $\mathbf{2}$, and a similar process occurring with $\mathrm{Ir}_{4}(\mathrm{CO})_{11}\left(\mathrm{PPh}_{3}\right)$ would yield 3 .

It has not yet been possible to synthesize the compounds $\mathbf{1 - 3}$ by other methods. We believe that reactions of [OSn-$\left.\mathrm{R}_{3}\right]^{-}$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 transitionmetal catalysts. Further studies of the reactions of $\mathrm{Ph}_{3} \mathrm{SnOH}$
with transition-metal carbonyl complexes in basic media are in progress.

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Supporting Information Available: Text, a table, figures, and CIF files giving details for the synthesis of compounds $\mathbf{1 - 3}$ 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.


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