

## Chapter 24

### New Applications of Electrophilic Aromatic C–H Activation with Metal Trifluoroacetates

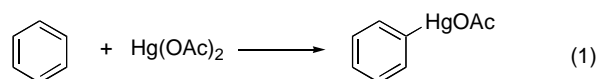
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New synthetic applications have been found for high oxidation state trifluoroacetato (TFA) complexes of Rh, Sn, and Ir. Highly selective oxidative carbonylation of arenes has been carried out with "Rh(TFA)<sub>3</sub>" catalyst under mild conditions (20-65 °C, 1 atm) to produce carboxylic acids via C-H activation. The first intermolecular electrophilic stannylation of arenes has been performed with Sn (IV) TFA species generated from Sn (II) oxide or tetraphenyltin. A new simple method has been developed for exhaustive cyclometalation of fluorinated 2-arylpyridines with Ir (III) TFA complexes to produce tricyclometalated derivatives which are among the most efficient electroluminescent materials known to date.

To the best of our knowledge, the first example of C-H activation with a metal compound is the aromatic electrophilic mercuration reported by Dimroth as early as 1898 (1). In a series of his articles published in 1898-1902 (1, 2) Dimroth described the preparation of a number of arylmercury acetates from  $\text{Hg}(\text{OAc})_2$  and various aromatic hydrocarbons (e.g., eq 1).



The electrophilicity of Hg (II) in such  $\text{S}_{\text{E}}\text{Ar}$  mercuration reactions can be enhanced dramatically by replacing the acetate of  $\text{Hg}(\text{OAc})_2$  with a less nucleophilic anion and by running the reaction in a more ionizing, poorly coordinating medium. At the same time, the counter-anion must be basic enough to successfully deprotonate the Wheland intermediate ( $\sigma$ -complex) to restore aromaticity in the final step of the process (3). Trifluoroacetate (TFA) appears to be an excellent counterion to meet both criteria. Thus, mercury trifluoroacetate ( $\text{Hg}(\text{TFA})_2$ ) in trifluoroacetic acid (TFAH) mercurates benzene  $6.9 \times 10^5$  times faster than the classical  $\text{Hg}(\text{OAc})_2 - \text{AcOH}$  system (4). Furthermore, Kampel et al. have found (5) that icosahedral carboranes readily undergo mercuration with  $\text{Hg}(\text{TFA})_2$  in TFAH under mild conditions, while remaining totally unreactive toward  $\text{Hg}(\text{OAc})_2$  in AcOH even at elevated temperatures. Deacon and Farquharson (6) have demonstrated that up to 5 Hg atoms can be introduced into the benzene ring with  $\text{Hg}(\text{TFA})_2$ , whereas  $\text{Hg}(\text{OAc})_2$  can afford only the monomercurated product.

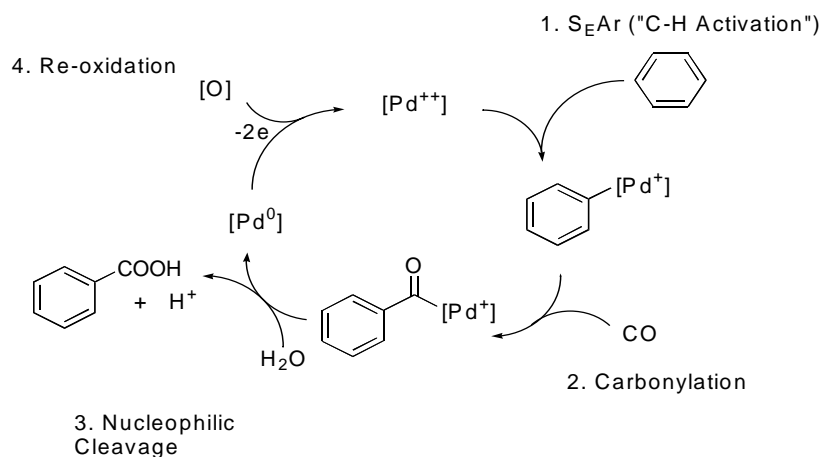
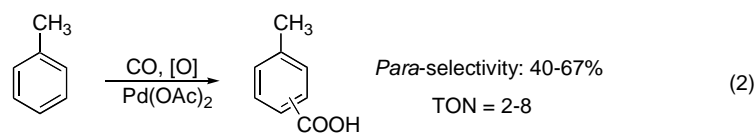
We used the above considerations for the development of a series of new applications of metal TFA complexes in synthesis and catalysis. The three sections below describe (i) a new Rh catalytic system for oxidative carbonylation of aromatic hydrocarbons via C-H activation under mild conditions, (ii) the first direct intermolecular stannylation of arenes, and (iii) a simple, novel synthesis of new, highly photo- and electroluminescent tricyclic metalated Ir complexes of fluorinated 2-arylpyridines.

### Rh-Catalyzed Oxidative Carbonylation of Arenes under Mild Conditions

Finding an efficient catalytic system to directly introduce a small  $\text{C}_1$  or  $\text{C}_2$  group (e.g.,  $\text{CH}_3$ ,  $\text{CH}_2\text{OH}$ ,  $\text{CHO}$ ,  $\text{COOH}$ ,  $\text{C}_2\text{H}_5$ ,  $\text{CH}=\text{CH}_2$ , etc.) in the *para*-position of toluene represents a considerable intellectual and practical challenge. Such *para*-substituted toluenes could be cleanly oxidized to terephthalic acid, an important monomer for polyester (7). Terephthalic acid is currently produced from *p*-xylene which is significantly more costly than toluene.

Scientifically, upon initial consideration the problem of catalytic introduction of *any* carbon substituent into the *para* (not *meta*!) position of toluene might look like an easy one. Nonetheless, there have been no reports of a catalytic reaction that would furnish a *para*-C-derivative of toluene directly from toluene with high selectivity and a satisfactory catalytic turnover number (TON).

In principle, the Fujiwara reaction (8), also known as oxidative carbonylation of arenes, (eq 2) might provide a solution to the synthesis of toluic acids from toluene and carbon monoxide. However, the *para*-selectivity of the Pd-catalyzed oxidative carbonylation of toluene is in the range of only 40-67%, with low TON (< 10) even under optimized conditions (8).



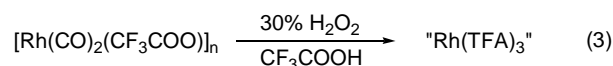
**Scheme 1**

A widely accepted mechanism for the Fujiwara reaction includes the electrophilic attack of  $Pd^{2+}$  on the aromatic ring, followed by migratory insertion

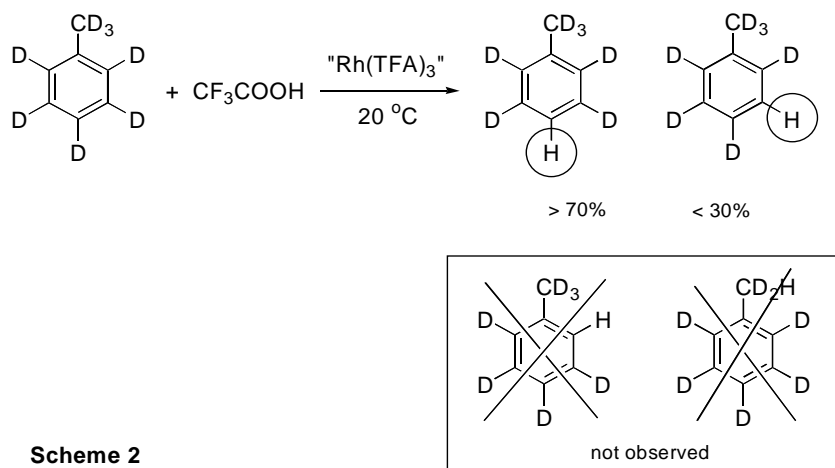
and nucleophilic cleavage to give a molecule of the acid and Pd (0). The latter must be re-oxidized to the catalytically active Pd (II) which then can commence another catalytic turnover (Scheme 1).

Oxidative carbonylation of toluene has also been performed (9, 10) in the presence of Rh catalysts with higher *para*-selectivities occasionally reaching 90+%. Conditions required for these Rh-catalysed reactions to occur are harsh, up to 270 atm of CO/O<sub>2</sub> at 150 °C. It was not clear if such severe conditions were needed for the C-H activation step or metal re-oxidation.

Keeping in mind the mercury trifluoroacetate chemistry (see Introduction) we intended to develop a rhodium-based catalytic system devoid of strongly coordinating anions. A material formulated as rhodium (III) trifluoroacetate, "Rh(TFA)<sub>3</sub>", (11) appeared promising but contamination with strongly-binding chloride (12) greatly diminished the electrophilicity of Rh<sup>3+</sup> and its ability to attack the benzene ring (see above). To eliminate the Cl<sup>-</sup> contamination problem, we found (12, 13) a new method to prepare genuinely Cl-free "Rh(TFA)<sub>3</sub>" by exhaustive oxidation of [Rh(CO)<sub>2</sub>(CF<sub>3</sub>CO<sub>2</sub>)<sub>n</sub>] with H<sub>2</sub>O<sub>2</sub> in TFAH (eq 3).



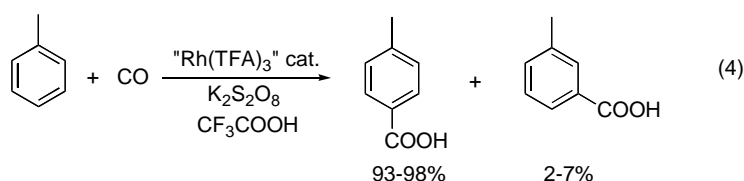
The product of this oxidation was found (12) to efficiently catalyze H/D exchange between trifluoroacetic acid and benzene-*d*<sub>6</sub> or toluene-*d*<sub>8</sub> (Scheme 2).



**Scheme 2**

The expected electrophilic mechanism of this H/D exchange was supported by (i) strong inhibition by chloride, observed upon addition of  $[(\text{Ph}_3\text{P})_2\text{N}]^+ \text{Cl}^-$  ( $[\text{PPN}]^+ \text{Cl}^-$ ) and (ii) the positional selectivity observed for the reaction of  $\text{CD}_3\text{C}_6\text{D}_5$  with  $\text{CF}_3\text{COOH}$ . Exchange occurred at the *ortho* (major) and *meta* (minor) positions of the toluene molecule (Scheme 2) without involving the *ortho*-position or the  $\text{CD}_3$  group. Due to fast rates and multiple exchange we could only roughly estimate the selectivity at  $> 70\%$  *para* and  $< 30\%$  *meta* (12).

When “ $\text{Rh}(\text{TFA})_3$ ” was tested as a catalyst to oxidatively carbonylate toluene in a 1 : 1 (by volume) mixture with trifluoroacetic acid using  $\text{K}_2\text{S}_2\text{O}_8$  as an oxidant, the reaction (eq 4) occurred under exceedingly mild conditions, 1 atmosphere of CO and 20-65 °C (12, 13). In accord with the results of the H/D exchange experiments, the selectivity for the desired *p*-toluic acid was in the range of 93-98%, the remaining 2-7% being *m*-toluic acid. No carboxylation occurred at the  $\text{CH}_3$  group or the *ortho*-positions of the ring. The reaction was catalytic in Rh, with TON = 40-100.



The most remarkable characteristics of the catalytic process (eq 4) are the particularly mild conditions and consistently very high *para*-selectivity. Further studies revealed a number of important features (12):

- Under identical conditions, *lower* catalyst concentrations resulted in *higher* turnover numbers (Figure 1).
- The reaction slowed down as CO pressure was increased.
- The catalyst tolerated the reaction products,  $\text{KHSO}_4$  and toluic acid.
- Small amounts of water did not poison the catalyst, whereas chloride did.
- The *para*-selectivity was consistently in the range of 93-98% whether the reaction was run at 20, 50 or 65 °C.
- The determined kinetic isotope effect of 3 was high, possibly due to a bulky metal electrophile acting under strongly acidic conditions (TFAH).
- Toluene was ca. 2 times more reactive than benzene.
- No reaction was observed in acetic acid.
- No oxidative carbonylation of toluene took place in the presence of  $\text{C}_6\text{Me}_6$ , probably due to the formation of stable  $[(\text{C}_6\text{Me}_6)\text{Rh}(\text{CO})_2]^+$  (see below).
- The readily available Rh (II) trifluoroacetate dimer  $[\text{Rh}_2(\text{TFA})_4]$  exhibited very low catalytic activity, if any.

Considering the above observations, it is believed that the first step of the catalytic process involves electrophilic attack of a Rh (III) TFA complex on the benzene ring to form a Rh aryl which then undergoes carbonylation (Scheme 3). The structure of the reactive Rh species remains unknown but the oxidation state of +3 suggests that the coordination number on the metal is probably 6 in the resting state and 5 for the reactive electrophilic form. Therefore, the active Rh electrophile is expected to be a bulky species, which accounts for the high para-selectivity of the process. Although the Rh center of the electrophile is too electron-deficient to strongly interact with CO, it is reasonable to propose some weak, reversible interactions between the two (Scheme 3). At higher CO concentration the equilibrium would be shifted toward less electrophilic Rh (III) carbonyl species, thus rationalizing slower rates at increased CO pressures.

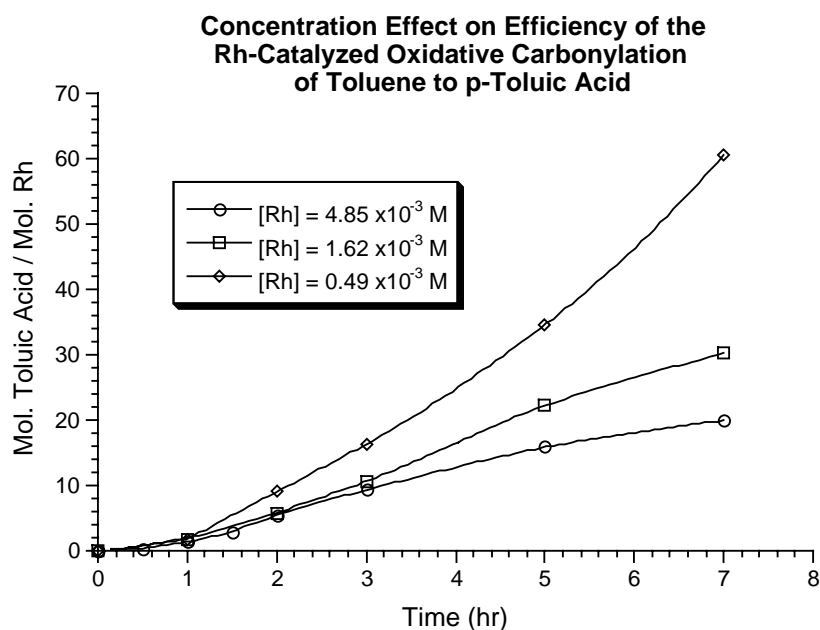
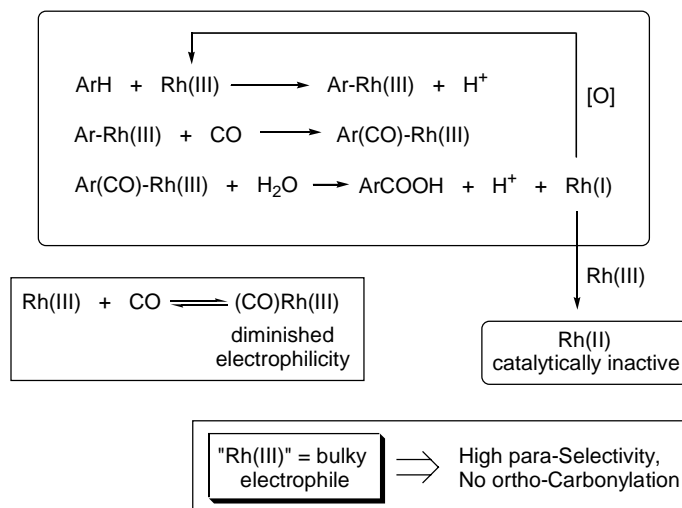


Figure 1. *Higher TONs are obtained with lower concentrations of Rh catalyst.* (Reproduced from reference 12. Copyright 2001 Wiley-VCH).

In the final step (Scheme 3) an aroyl Rh complex reacts with a suitable nucleophile, such as water or trifluoroacetate anion to give the aromatic acid or

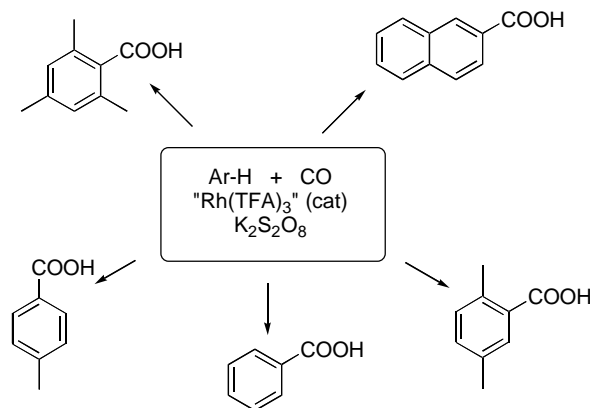
its mixed anhydride along with Rh (I). The latter is oxidized back to Rh (III) to close the catalytic loop. As the process occurs, the reaction mixture contains both Rh (I) and Rh (III) species which may comproportionate to produce the stable and catalytically inactive Rh (II) dimer (see above). It is believed that it is the comproportionation side process  $\text{Rh(I)} + \text{Rh(III)} \rightarrow 2\text{Rh(II)}$  that deactivates the catalyst, and is an important factor responsible for more efficient catalysis at lower Rh concentrations (Figure 1).



**Scheme 3**

Interestingly, hexamethylbenzene was found to poison the Rh catalyst, possibly due to the formation of oxidation-resistant  $[(\text{C}_6\text{Me}_6)\text{Rh}(\text{CO})_2]^+$ . As was demonstrated by a separate experiment (12), strong acids favor the reversible formation of  $[(\eta^6\text{-arene})\text{Rh}(\text{CO})_2]^+$  from  $[(\text{CO})_2\text{Rh}(\text{TFA})]_n$ . The arene Rh (I) complex undergoes very slow oxidation by  $\text{H}_2\text{O}_2$  in TFAH at room temperature, possibly via a small equilibrium concentration of  $[(\text{CO})_2\text{Rh}(\text{TFA})]_n$ . Hexamethylbenzene is expected to bind to Rh (I) more strongly, thus inhibiting the re-oxidation step.

Using our catalytic system we also synthesized aromatic carboxylic acids from a number of other arenes (Scheme 4). As can be seen from Scheme 4, the C-H activation *ortho* to a methyl group and even two methyl groups appears possible. At the same time, the carboxylation of naphthalene was at least 97%  $\beta$ -selective, indicating that steric effects play an important role in the reaction.

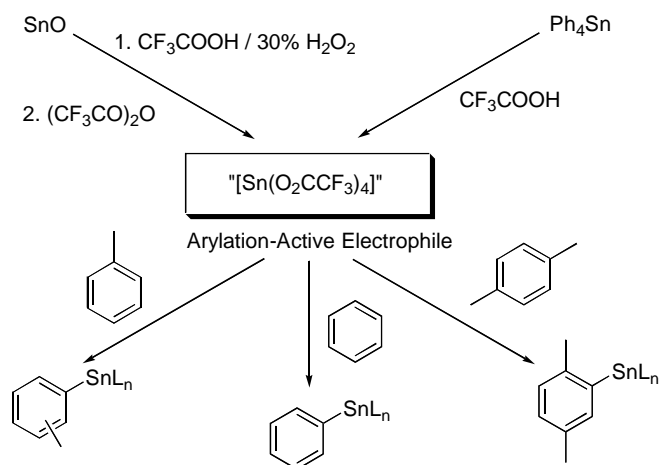


Scheme 4

### Electrophilic Stannylation of Arenes

The direct electrophilic metalation of arenes (e.g., eq 1) is clearly the simplest and most economical route to aryl derivatives of the main group elements, which are widely used in synthesis. Besides mercury (II) (1-6, 14) (see the Introduction), only two other main group metals, thallium (III) (15) and lead (IV) (16) form salts which are capable of direct intermolecular electrophilic metalation of aromatics under mild conditions (17). Adding tin to this list was desirable because of the importance of organotin compounds. "Tin has a larger number of its organometallic derivatives in commercial use than any other element" (18).

Reactivity considerations outlined in the Introduction made us believe that TFA complexes of Sn (IV) should be promising candidates for direct electrophilic aromatic stannylation. First it was found (19) that exhaustive dephenylation of Ph<sub>4</sub>Sn with TFAH resulted in a TFA Sn (IV) species which indeed activated aromatic C-H bonds of benzene, toluene, and *p*-xylene to give aryltin derivatives. We then also developed another route to this electrophilic tin species by oxidizing readily available and inexpensive SnO with 30% hydrogen peroxide in trifluoroacetic acid, followed by treatment with trifluoroacetic anhydride (19). Reactions of the thus prepared Sn (IV) electrophilic reagent with arenes afforded organotin compounds which were isolated and fully characterized in the solid state and in solution (Scheme 5).



Scheme 5

All attempts to isolate and characterize an analytically pure single compound from the arylation-active material were unsuccessful. It is believed that the electrophilic species may consist of mixtures of Sn(CF<sub>3</sub>COO)<sub>4</sub> and trifluoroacetoxy-polystannoxanes such as the hypothetical tetramer Sn<sub>4</sub>(μ<sup>3</sup>-O)<sub>2</sub>(CF<sub>3</sub>COO)<sub>12</sub> analogous to the aryltin stannylation products (see below). Although the electrophilic stannylation reactions are reversible (<sup>1</sup>H NMR), the equilibrium can be shifted towards the desired aryltin product by running the reaction with arene under reflux for 5-10 minutes. Thus, the compound [(Ph)<sub>2</sub>Sn<sub>4</sub>O<sub>2</sub>(CF<sub>3</sub>COO)<sub>10</sub>] was the main phenyltin species isolated from the reaction of benzene with SnO-derived "trifluoroacetato-tin (IV)" (Equation 5).

The structure of this organotin cluster was established as [Sn<sub>4</sub>(Ph)<sub>2</sub>(μ<sup>3</sup>-O)<sub>2</sub>(μ-CF<sub>3</sub>COO)<sub>6</sub>(η<sup>2</sup>-CF<sub>3</sub>COO)<sub>2</sub>(η<sup>1</sup>-CF<sub>3</sub>COO)<sub>2</sub>] by X-ray diffraction (Figure 2) (19). The presence of the Ph-Sn bond in solution was confirmed by the observation of Sn-H coupling to the *ortho* protons with <sup>3</sup>J<sub>Sn-H</sub> = 177 Hz. A broadened singlet in the <sup>19</sup>F NMR spectrum of the sample indicated that the cluster was fluxional at ambient temperature, probably undergoing fast exchange of the TFA ligands. Bromination of the isolated material led to the clean formation of bromobenzene in 91% yield, assuming that [(Ph)<sub>2</sub>Sn<sub>4</sub>O<sub>2</sub>(CF<sub>3</sub>COO)<sub>10</sub>] was the only Ph-Sn species present in the bulk product. This assumption, however, is made cautiously as other phenyl tin species may be present in the crude isolated material.

Similarly, direct stannylation of *para*-xylene was carried out (19). The structure of the *p*-xylyl Sn complex is very similar to the phenylated compound, but there is also a remarkable difference between the two. In the phenyl derivative (Figure 2), the "organometallic" tin atoms are seven-coordinate, being

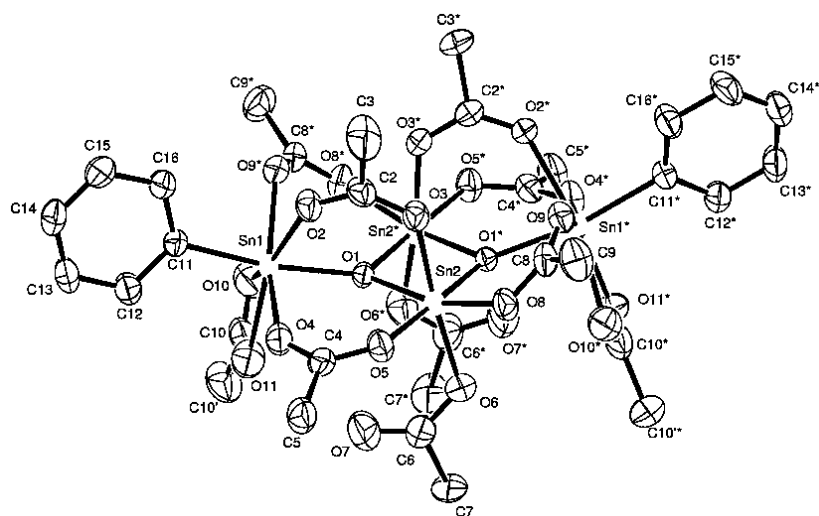
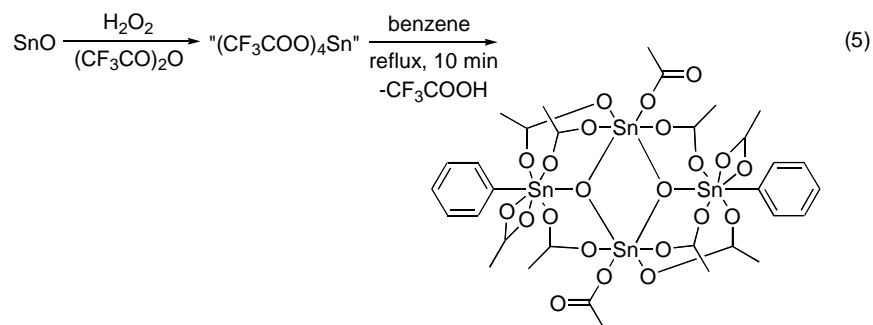
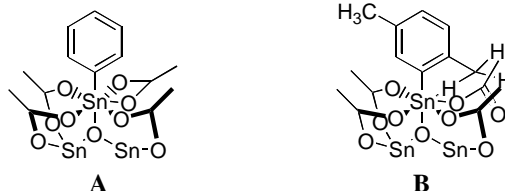


Figure 2. An ORTEP drawing of  $[\text{Sn}_4(\text{Ph})_2(\mu^3\text{-O})_2(\mu\text{-CF}_3\text{COO})_6(\eta^2\text{-CF}_3\text{COO})_2(\eta^1\text{-CF}_3\text{COO})_2]$  obtained via the direct stannylation of benzene. Fluorine atoms are omitted for clarity. (Reproduced from reference 19. Copyright 2001 Wiley-VCH).

surrounded by one carbon and six oxygens of the  $\mu$ -oxo and TFA ligands (**A**; F atoms are omitted). surrounded by one carbon and six oxygens of the  $\mu$ -oxo and TFA ligands (**A**; F atoms are omitted). In the xylyl complex however, there are only five oxygens in the first coordination sphere of the arylated tin atom, but the octahedron is distorted, due in part to interaction between the metal and the *ortho*-methyl group (**B**; F atoms are omitted). The non-bridging trifluoroacetate ligand in the phenyl complex is  $\eta^2$ , whereas in the xylyl compound it is  $\eta^1$ .



When toluene was stannylated, a mixture of organotin compounds formed. The positional selectivity of this reaction ( $^{13}\text{C}$  NMR and bromination studies) was surprising, the *ortho* : *meta* : *para* ratio was ca. 0 : 2 : 1 (19). The observed lack of stannylation at the *ortho* positions is likely due to steric bulk of the reactive Sn electrophile, whereas the *meta* to *para* ratio of 2 is uncommon but not unprecedented in  $\text{S}_{\text{E}}\text{Ar}$  chemistry, pointing to exceptionally high reactivity of the acting electrophile (20).

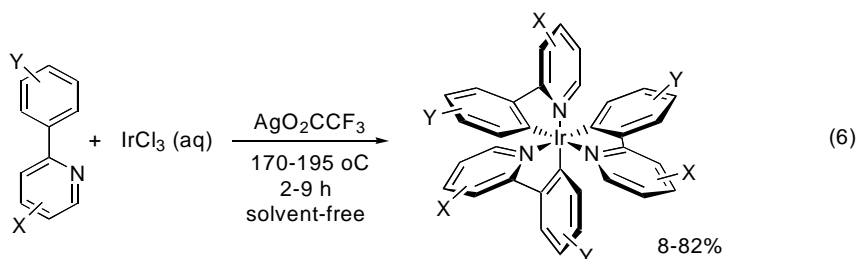
In concluding this section, tin has now been added to the list of main group metals (Hg, Tl, and Pb) which form compounds capable of directly electrophilically metalating arenes at mild temperatures.

### One-Step Synthesis of Highly Luminescent Triply Cyclometalated Organometallic Iridium Complexes of Fluorinated 2-Arylpyridines

It is currently believed that organic light emitting diodes (OLEDs) may dominate the display industry of the future. The tricyclic metalated iridium complex of 2-phenylpyridine  $[\text{Ir}(\text{ppy})_3]$  originally described and studied by Watts (21), has been recently identified as a green emitter of unprecedented efficiency (22). We decided to synthesize fluorinated analogues of  $[\text{Ir}(\text{ppy})_3]$  which we expected to exhibit improved electroluminescent and processing properties, such as volatility and thermal stability.

The reaction of 2-phenylpyridine with  $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$  readily produces a non-luminescent doubly cyclometalated Cl-bridged dimer (21, 23, 24). The third cyclometalation which affords the desired luminescent compound  $[\text{Ir}(\text{ppy})_3]$  occurs only sluggishly and usually in low yield under aggressive conditions, even if performed on pre-isolated dicyclic metalated intermediate in the presence of silver triflate (24).

Having prepared a series of fluorinated 2-arylpyridine derivatives via Suzuki-Miyaura coupling (25, 26), we were in need of a simple, efficient, and preferably one-step method for their triple cyclometalation with Ir (III). Although mechanistic details of the cyclometalation of 2-phenylpyridine with  $\text{IrCl}_3$  were unknown, the oxidation state of the metal and some of our preliminary experimental observations suggested an  $\text{S}_{\text{E}}\text{Ar}$ -type mechanism for the C-H activation. Therefore, we thought that converting chloro iridium intermediates into their more electrophilic TFA analogues (see above) should



X = H; Y = H, 2-F, 4-F, 3-CF<sub>3</sub>;  
 X = 5-CF<sub>3</sub>; Y = H, 2-F, 3-F, 4-F, 3-CH<sub>3</sub>O, 4-CH<sub>3</sub>O, 3-CF<sub>3</sub>, 4-CF<sub>3</sub>O;  
 X = 3-Cl; Y = 3-CF<sub>3</sub>;  
 X = 5-NO<sub>2</sub>; Y = 3-CF<sub>3</sub>;

facilitate the metalation. Indeed, we were pleased to find (25, 26) that iridium (III) chloride readily reacted with the 2-arylpiperidines in the presence of 3 equivalents of AgOCOCF<sub>3</sub> to produce the desired tri-cyclometalated complexes in up to 82% yield (eq 6). The reaction is run in excess arylpiperidine ligand which is easily recovered and recycled after the reaction.

Our recycling technique allowed for the synthesis on a considerable scale, i.e. an excellent green emitter (25-27) shown in Figure 3 was made in the amount of 55 grams (99.98% purity) in 70% yield calculated on the ligand and iridium chloride used. The fluorinated iridium complexes easily sublimed without any sign of decomposition, a critical property for vacuum-deposition technology. Importantly (27), the complexes exhibited very high electroluminescent efficiencies in pure films *without* the host matrix (25-27) which is required (22) for the parent [Ir(ppy)<sub>3</sub>] complex.

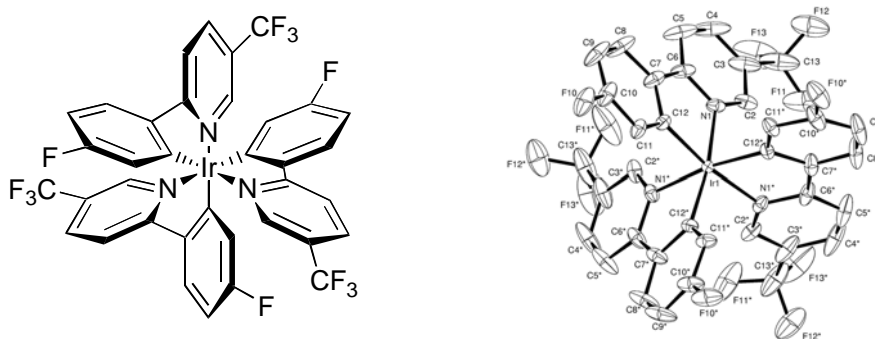


Figure 3. Structural formula and an ORTEP drawing for the most efficient green emitter synthesized via the TFA method (eq 6). (The ORTEP reproduced from reference 25. Copyright 2001 The Royal Chemical Society).

Exploiting the generality of the TFA method, we succeeded in preparing numerous complexes containing different substituents in different positions of the aromatic rings (eq 6). The availability of a large series of the materials led to a better understanding of how molecules of this type should be designed for color tuning via systematic control of the nature and position of the substituents (25), a key issue for the technology of full color displays of the future. Further details of our electroluminescent studies can be found elsewhere (25-27).

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