

Selective One-pot Synthesis of Facial Tris-ortho-metallated Iridium(III) Complexes Using Microwave Irradiation

Hideo Konno* and Yoshiyuki Sasaki

National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569

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We report on a novel synthesis method for the production of two facial tris-ortho-metallated iridium(III) complexes, *fac*-[Ir(ppy)₃] (**1a**; ppyH = 2-phenylpyridine) and *fac*-[Ir(tpy)₃] (**1b**; tpyH = 2-(*p*-tolyl)pyridine), by the reaction of IrCl₃·3H₂O with a large excess of the corresponding 2-arylpyridine under microwave irradiation. The method does not require a dehalogenating reagent such as AgCF₃SO₃, and facial tris-ortho-metallated iridium(III) complexes can be obtained rapidly, selectively and efficiently.

Transition metal complexes, especially iridium(III) complexes with 2-arylpyridine ligands such as *fac*-[Ir(ppy)₃] (**1a**; ppyH = 2-phenylpyridine) have attracted much attention as phosphors for organic light-emitting diodes (OLEDs).¹ Such iridium(III) complexes can emit efficiently from triplet metal-to-ligand charge transfer (³MLCT) and/or by a ³π-π* transition on the ligand excited state, even at ambient temperature, because of efficient singlet-triplet mixing.^{2,3} In addition, the theoretical limit of the quantum efficiency of electroluminescence (EL) becomes three times higher when using phosphorescent compounds rather than fluorescent compounds such as aluminum tris(8-hydroxyquinoline).¹

Several tris-ortho-metallated iridium(III) complexes with various organic ligands have already been reported by other research groups.² Although iridium chloride reacts with 2-arylpyridine under reflux conditions, the undesired dichloro-bridged dimer (**2**)^{3c,3e} is the main product, with only a small amount of the tris-ortho-metallated complex (10%).³ It has been reported that both the addition of a dehalogenating reagent such as AgCF₃SO₃ and refluxing for several hours are "essential" for the synthesis of tris-ortho-metallated complexes, even though the yield is still low and a troublesome procedure is required to separate the desired complexes from the precipitated AgCl.^{2a,2e}

In recent years there has been an ever growing interest in the application of microwave irradiation as a new technology for the synthesis of both metal complexes⁴ and organic compounds.⁵ We report here the rapid and selective one-pot synthesis of facial tris-ortho-metallated iridium(III) complexes (**1**)^{3a,3b} under microwave

Table 1. Comparison of this work and prior procedures for the synthesis of **1a**.

No.	Substance	Time/min	Additive	Yield ^a /%
1 ^b	IrCl ₃ ·3H ₂ O	1	none	75
2 ^c	IrCl ₃ ·H ₂ O	1440	none	10
3 ^d	IrCl ₃ (aq)	120–540	AgCF ₃ CO ₂	25
4 ^e	[Ir(ppy) ₂ Cl] ₂	1440	AgCF ₃ SO ₃	75 ^f
5 ^g	Ir(acac) ₃ ^h	600	none	45 ⁱ

^aIsolated yield. ^bThis work. ^cRef. 3b. ^dRef. 2a. ^eRef. 2e. ^fThe reported yield of [Ir(ppy)₂Cl]₂ from IrCl₃·H₂O is 72%.^{3c}

^gRef. 3a. ^hacacH = acetylacetone. ⁱThe reported yield of Ir(acac)₃ from IrCl₃·nH₂O is 45%.⁸

irradiation. This new synthetic route does not require a dehalogenating reagent or column chromatographic operation for purification.

In a typical run, an ethylene glycol solution (10 ml) containing 2-phenylpyridine (14 mmol) and IrCl₃·3H₂O (0.14 mmol) in a round-bottom flask was irradiated with microwave (2450 MHz) under an Ar atmosphere for 1 min.⁶ The resulting yellow solution was evaporated to ca. 5 ml under reduced pressure to precipitate yellow solids, which were collected by filtration, washed with water followed by pentane, and then dried in vacuo.⁷ Pure **1a** was obtained in 75% yield, which is much higher than that obtained in previously reported syntheses of **1a**. Table 1 clearly shows that the microwave synthesis of **1a** (No. 1) is superior to conventional methods (No. 2–5), that is, it gives higher yield, has a shorter reaction time, does not require a dehalogenating reagent and employs a simple post-treatment.

Table 2 summarizes the distribution of the formation of **1** and **2** under various experimental conditions. It should be noted that the product distribution was strongly dependent on the amount of 2-arylpyridine in the solution. When a large excess of 2-arylpyridine (50–100 times molar excess) was used, **1** was produced quantitatively after microwave irradiation for several min (No. 1, 2, 4). In the initial stages of the reaction (within 1 min for No. 3), the dichloro-bridged dimer (**2a**) was detected but this disappeared after 3 min of microwave irradiation (No. 4). These results suggest that **2** could be one of the precursors of **1**. In fact, **1** could be produced quantitatively by the microwave reaction of **2**, which was prepared separately according to the method in the literature,^{3d} with 2-arylpyridine (50 times excess) in ethylene glycol.

However, under a 10–30 times excess of the corresponding 2-arylpyridine (No. 5–7), 45–100% of **2** remained, even after microwave irradiation for 30 min. This indicates that 2-arylpyridines, i.e., ppyH and tpyH, act not only as a ligand but also as a base to trap protons in the solution. Since the deprotonation process from 2-arylpyridine is essential for coordination to the

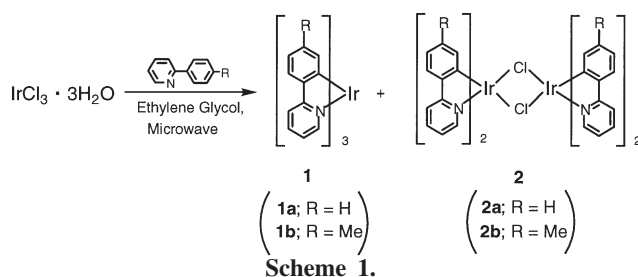


Table 2. Synthesis of the ortho-metalated iridium(III) complex by microwave irradiation [Scheme 1].

No.	R	Ligand (eq ^a)	Irradn. time/min	Ratios 1:2 ^b
1	H	ppyH ^c (100)	1	100:0
2	Me	tpyH ^d (100)	3	100:0
3	H	ppyH (50)	1	90:10
4	H	ppyH (50)	3	100:0
5	H	ppyH (30)	30	55:45
6	H	ppyH (10)	30	0:100
7	Me	tpyH (10)	30	0:100

^aMolar ratio of the ligand vs. IrCl₃·3H₂O used. ^bRatios determined from the integrals of the ¹H NMR spectra. ^cppyH = 2-phenylpyridine. ^dtpyH = 2-(*p*-tolyl)pyridine.

iridium(III) center, a base should be required for the one-pot synthesis of **1**. Actually, in the presence of Na₂CO₃, only 30 times excess of 2-arylpyridine was enough to produce **1** selectively.⁹

In conclusion, the ortho-metalated iridium complexes (**1a**) can be efficiently obtained by the reaction of IrCl₃·3H₂O with a large excess of the corresponding 2-arylpyridine under microwave irradiation without using a dehalogenating reagent, and this synthetic method can probably be applied to other ortho-metalated iridium complexes for organic light emitting diode devices (OLEDs).

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References and Notes

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- We used the experimental apparatus consisting of a domestic microwave oven with a reflux condenser as reported by Matsumura et al.^{4c}
- The purities of the synthesized complexes were confirmed by ¹H NMR (500 MHz).^{2e,3c,3e} **1a**: Isolated Yield 75%. **1b**: Isolated Yield 67%.
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