

Synthesis, structural characterization, and initial electroluminescent properties of bis-cycloiridiated complexes of 2-(3,5-bis(trifluoromethyl)phenyl)-4-methylpyridine

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Abstract

A series of bis-cyclometalated Ir(III) complexes (**8–10**, **12**, **15**, **17**, **19**, **21**, **23**, **25**, **28**, **29** and **33**) bearing two chromophoric N[^]C cyclometalated ligands derived from 2-(3,5-bis(trifluoromethyl)phenyl)-4-methylpyridine (**1**) and a third nonchromophoric ligand has been synthesized. A palladium-catalyzed cross-coupling reaction between 2-chloro-4-methylpyridine (**2**) and 3,5-bis(trifluoromethyl)phenylboronic acid (**3**) was used to prepare 2-(3,5-bis(trifluoromethyl)phenyl)-4-methylpyridine (**1**). Cyclometalation of (**1**) by IrCl₃ was carried out in (MeO)₃P=O, with the formation of chloro-bridged dimer [N[^]C]₂Ir(μ-Cl)₂Ir[C[^]N]₂ (**8**). Reaction of (**8**) with lithium 2,4-pentanedionate, lithium 2,2,6,6-tetramethyl-heptane-3,5-dionate (**13**), dipivaloyltrimethylsilylphosphine (**14**), 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octadione (**16**), 1,1,1,3,3,3-hexafluoro-2-pyridin-2-yl-propan-2-ol (**18**), 1,1,1,3,3,3-hexafluoro-2-pyrazol-1-ylmethyl-propan-2-ol (**20**), 2-diphenylphosphanylethanol (**22**), and 1-diphenylphosphanylpropan-2-ol (**24**), afforded octahedral iridium complexes **9**, **12**, **15**, **17**, **19**, **21**, **23** and **25**, respectively. Complex **10**, which contains three different ligands (L₁ = N[^]C of **1**; L₂ = N[^]C of 4,4'-dimethyl-[2,2']bipyridinyl **4**; L₃ = O[^]O of 2,4-pentanedione), and complex **11**, which contains no cyclometalated ligands (L₁ = **4**; L₂ = L₃ = Cl; L₄ = O[^]O of 2,4-pentanedione) were also isolated as minor products in a one-pot reaction between a 94:5 mixture of **1** and **4**, IrCl₃ and lithium 2,4-pentanedionate. Reaction of **8** with diphenylphosphanylmethanol (**27**) in 1,2-dichloroethane unexpectedly led to complexes **28** and **29**. The reactions of **8** with benzoylformic acid resulted in the formation of hydroxyl-bridged dimer [N[^]C]₂Ir(μ-OH)₂Ir[C[^]N]₂ (**33**). According to X-ray analyses, Ir-to-Ir distances in the crystal cell increase from 6.86 Å for **10** to 13.31 Å for **33**. The angle theta, which represents the twisting of two cyclometalated C–Ir–N planes relative to each other, varies from 97.5° for **21** to 90.76° for complex **28**. OLED devices were fabricated from several Ir complexes and preliminary results are discussed.

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1. Introduction

Smithson Tennant discovered the element iridium over 200 years ago in the black residues remaining from the treatment of platinum ores [1]. Since then iridium has been linked to phenomena ranging from the disappearance of dinosaurs [2] to organic light emitting diodes [3]. In partic-

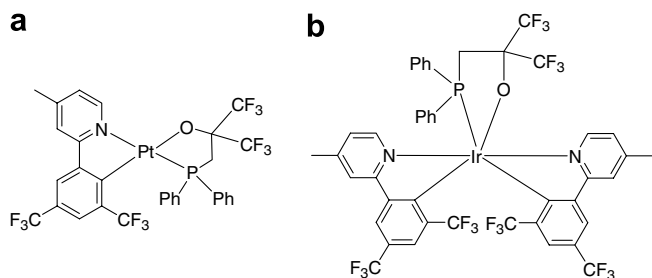
ular, mono-cyclometalated (N[^]C) Pt^{II} complexes (Type **a** in the **Scheme 1**) and bis-cyclometalated (N[^]C) complexes of Ir^{III} with 2-phenylpyridine ligands (Type **b** in the **Scheme 1**) have been widely investigated as promising electroluminescent materials for OLED applications.

Emission colors from these Pt and Ir complexes range from blue-green, to green and to red, and depend mostly on the choice of the chromophoric cyclometalated ligand. The electronic parameters and steric bulk of the second, nonchromophoric ligands are also important for the color coordinate and intensity of the emission. For example,

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Scheme 1.

increasing the steric bulk of the secondary auxiliary ligands in Pt-complexes (Type **a** in Scheme 1) shifted the emission wavelength to higher energies (from 600 nm to 540 nm) [4]. Introduction of P⁺O ligands was found to shift the emission to the blue part of the spectrum [5]. Blue emissive materials are among the most sought after components for the emerging OLED market.

In this report, we studied the effect of varying the third ligand in bis-cyclometalated Ir-complexes (Type **b** in Scheme 1). An attempt was made to correlate structural features of the bis-cyclometalated moiety of the iridium complexes with the final electroluminescent spectra. Such bis-cyclometalated iridium complexes are highly crystalline substances, which greatly facilitated X-ray analysis. Frequently, electrochemical and photochemical studies, as well as theoretical calculations, have been used to interpret the blue shift in OLED devices [3–5]. 2-(3,5-Bis(trifluoromethyl)-phenyl)-4-methylpyridine **1** was selected as a ligand for cycloiridation because it is easily prepared and it provides intensive blue emissive bis-cyclometalated Ir(III) complexes [5].

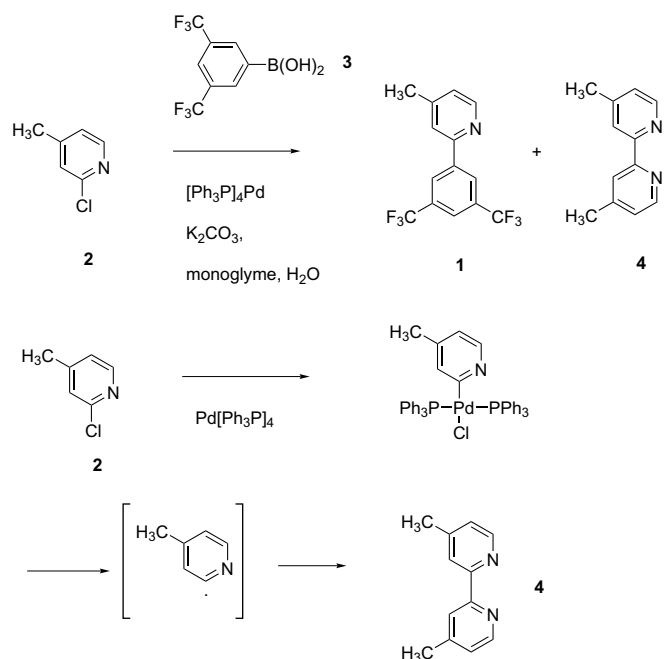
2. Results and discussion

2.1. Synthesis of bis-cyclometalated Ir(III) complexes and structural studies

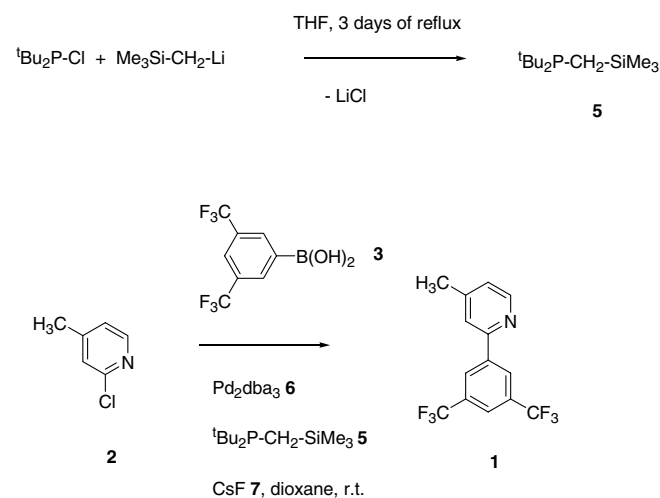
2.1.1. Synthesis of 2-(3,5-bis(trifluoromethyl)phenyl)-4-methylpyridine **1**

The palladium-catalyzed Suzuki cross-coupling reaction between 2-chloro-4-methylpyridine (**2**) and 3,5-bis(trifluoromethyl)phenylboronic acid (**3**) was used to prepare 2-(3,5-bis(trifluoromethyl)phenyl)-4-methylpyridine (**1**) (Schemes 2, 3). Two catalytic protocols were tested. The first one (Scheme 2) involves the tetrakis(triphenylphosphine)palladium(0) as the catalyst in the presence of potassium carbonate and a mixture of monoglyme (1,2-dimethoxyethane)/water as solvent. This protocol is attractive for its simplicity and the commercial availability of all reagents [6].

2-(3,5-Bis(trifluoromethyl)phenyl)-4-methylpyridine (**1**) was isolated by the distillation, together with some (<5%) 4,4'-dimethyl-[2,2']bipyridinyl (**4**). One explanation for the formation of compound **4** can be found in the general Suzuki catalytic cycle [6]. The intermediate formed by the



Scheme 2.



Scheme 3.

oxidative addition of 2-chloro-4-methylpyridine to tetrakis(triphenylphosphine)palladium(0) may undergo elimination of a 4-methylpyridinyl-2 radical with sequential dimerization to afford the 4,4'-dimethyl-[2,2']bipyridinyl (second reaction in Scheme 2). A second possibility is that 2-chloro-4-methylpyridine reacted with the first intermediate in the Suzuki reaction to yield 4,4'-dimethyl-[2,2']bipyridinyl.

Bipyridinyl **4** is able to participate in cyclometalation reactions, as was noted by Lepeltier and coauthors [7]. Consequently, an alternative synthesis of **1** was developed utilizing di-*tert*-butyl-trimethylsilylanyl methylphosphine (**5**) and Pd₂dba₃ **6** as the catalyst (Scheme 3). This catalytic protocol has proved to be quite reliable [8]. The di-*tert*-

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