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Phosphine-assisted bisbenzothienyl iridium(III) complexes: Synthesis, structures and photophysical properties

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ABSTRACT

Phosphine-assisted bisbenzothienyl iridium(III) compounds were synthesized and characterized, and their structures were confirmed through x-ray crystallography. The TG experiment showed that bisbenzothienyl iridium(III) compounds have excellent stability. In terms of photophysical properties, these complexes have the typical green emission.

The design and synthesis of the new Ir(III) complexes are currently of great interest because of their unique photophysical properties for OLED applications [1,2]. Among these complexes, the neutral ones are much more suitable for OLED applications than ionic iridium(III) complexes are, due to the process of vapor deposition [3,4]. Moreover, neutral complexes and particularly heteroleptic complexes are of interest because they typically exhibit outstanding optical properties [5,6].

Our research in organometallics is primarily focused on cyclometalated Ir(III) complexes, using amides as auxiliary ligands. Recently, we reported a number of amidate Ir(III) complexes containing phenylpyridyl (ppy) and phenylquinolyl (pq) cyclometalating ligands [7]. These complexes demonstrated photoluminescent efficiencies and color bands [8], but amide auxiliary ligands have not. Consequently, we must turn our attention to the search for other auxiliary ligands with which to synthesize the heteroleptic complexes and harness their excellent photophysical properties. Therefore, as part of our continuing study of auxiliary ligands, we report on our study of the synthesis, characterization, as well as the structural and photophysical properties of these phosphine-assisted bisbenzothienyl (bt) iridium(III) complexes.

According to the literature, dichloro-bridged complexes $[(bt)_2IrCl]_2$ have been synthesized from bt ligand with $IrCl_3 \cdot 3H_2O$. Subsequently, chloro-bridged dimer and phosphine ligand were placed in a Schlenk tube containing CH_2Cl_2 as solvent under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 6 h. After recrystallization, the $(bt)_2Ir(PAr_3)$ (**2**) complexes were obtained with moderate to good yields (Scheme 1) [9].

Crystal structure of 2a

Given the synthesis of phosphine-assisted bisbenzothienyl iridium(III) complexes, the molecular structure of **2a** was determined by x-ray diffraction, as shown in Fig. 1. Single-crystal analysis reveals that compound **2a** belongs to the $P2_1/c$ space group. Its crystallographic asymmetry unit contains one Ir complex (Fig. 1).

Meanwhile, the photophysical characterization of the $(bt)_2Ir(PAr_3)$ complexes (**2**) was explored (Fig. 2). The maximum absorption wavelengths of the complexes were observed at approximately 320 nm, being dramatically different from those of Ir(III) complexes with amides as auxiliary ligands.

The phosphorescence quantum yields (Φ_{PL}) of these Ir(III) complexes (**2**) were investigated at room temperature (as shown in Table 1). To our delight, the wavelengths of solution photoluminescence (PL) of complexes were observed at approximately 541 nm, which fall into the green-light region.

To determine the thermal stabilities of complexes, TG experiments were carried out and the thermal curves were as shown in Fig. 3. In most cases, the complexes showed a weight loss of approximately 10% at 300 °C, which is partially attributable to the oxidation of triphosphine. The experiment shows that these Ir(III) complexes with triphosphine ancillary ligand have good thermal stability.

Finally, with these complexes in hand, we want to expand their applications in the area of catalysis. The transfer dehydrogenation reaction of 1-phenylethanol with styrene was tested. First, we examined the

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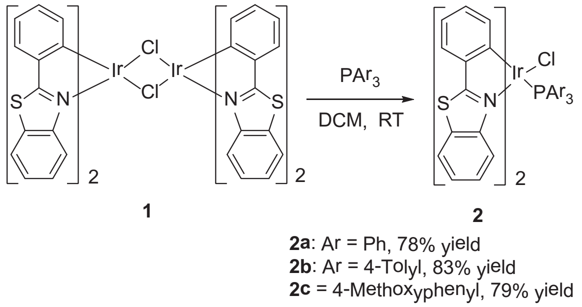


Scheme 1. Synthesis of phosphine-assisted bisbenzothienyl iridium(III) complexes.

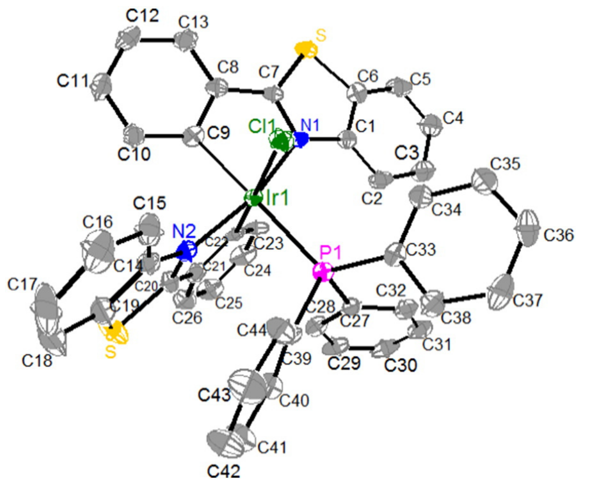


Fig. 1. ORTEP diagram of **2a** with thermal ellipsoids shown at the 30% probability level.

activity of these iridium complexes, and the results showed that the complex could catalyze the reaction but with a low yield. Next, the effects of base, solvent and temperature were all checked for the purpose of better yields (Table 2). The reaction was highly solvent-dependent. The yield of product was significantly lower in polar solvent, where toluene was found to be the most suitable one among the solvents tested.

Table 1
Photophysical properties of **2** complexes.[a]

Entry	Abs wavelength λ (nm)	Soln luminescence λ (nm)	Φ_{PL}
1	269, 318	541 (**2a**)	0.031
2	269, 322	539 (**2b**)	0.034
3	269, 319	543 (**2c**)	0.033

[a] Absorption and emission spectra were recorded in spectroscopic grade dichloromethane at 298 K. Quantum yields of emission were measured in degassed dichloromethane solutions, using Alq_3 in DMF (Φ_{PL} = 0.116) as a reference.

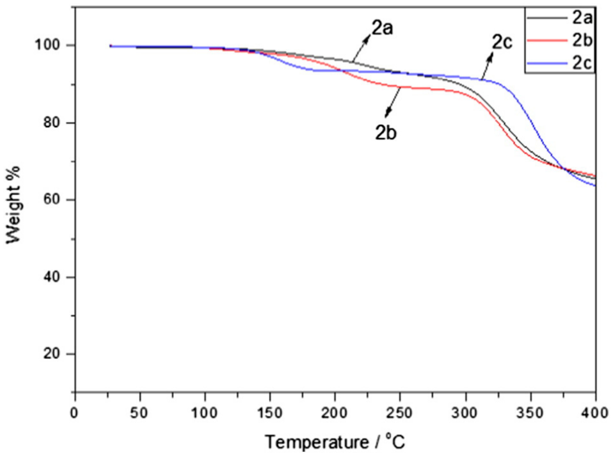


Fig. 3. Thermogravimetric curves of **2** complexes.

The result of the comparison of different bases suggested that the transfer dehydrogenation demands stronger basic sites. It should be noted that these experiments revealed that the bisbenzothienyl iridium(III) complexes (**2**) were feasible for the transfer dehydrogenation reaction with moderate yield. One point is that this shows us a direction to design and synthesize better catalysts for this transformation.

In conclusion, the phosphine-assisted bisbenzothienyl iridium(III) compounds were synthesized and characterized. X-ray crystallography confirmed the structure. The TG experiment showed that bisbenzothienyl iridium(III) compounds have excellent stability, and photophysical properties showed that these complexes gave the typical green emission. Further study on the catalytic reactivity and photophysical properties of these complexes is ongoing.

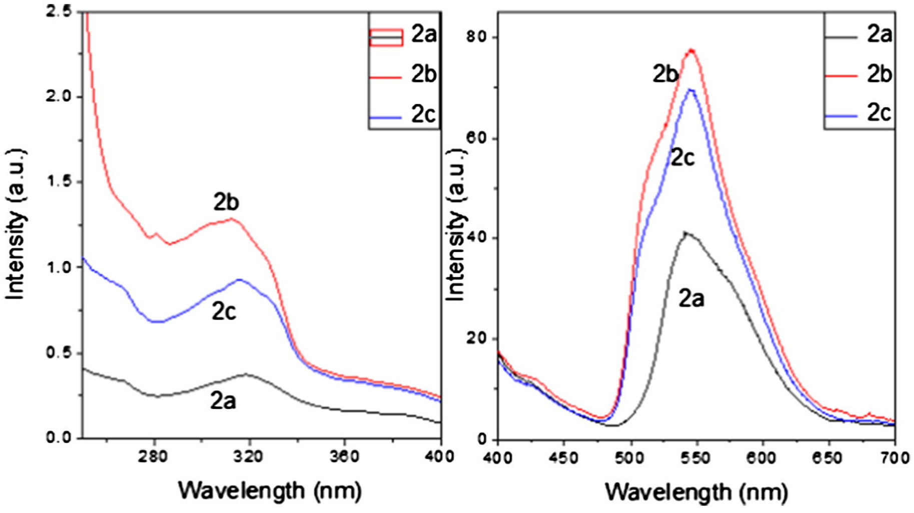
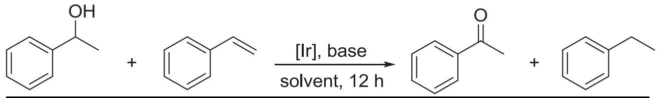


Fig. 2. UV–vis absorption and normalized PL emission spectra of complexes.

Table 2
Transfer dehydrogenation of 1-phenylethanol with styrene by bisbenzothienyl iridium(III) complexes (**2**).[a]



Entry	Catalyst	Base	Solvent	Temp. (°C)	Conv.%
1	**2a**	K_2CO_3	Toluene	110	31
2	**2b**	K_2CO_3	Toluene	110	33
3	**2c**	K_2CO_3	Toluene	110	35
4	**2c**	K_2CO_3	DMF	110	21
5	**2c**	K_2CO_3	DMSO	110	23
6	**2c**	KOH	Toluene	110	43
7	**2c**	*t*-BuOK	Toluene	110	59
8	**2a**	*t*-BuOK	Toluene	110	56
9	**2b**	*t*-BuOK	Toluene	110	54
10	**2c**	*t*-BuOK	Toluene	90	38
11	**2c**	*t*-BuOK	Toluene	130	52

[a] Reaction conditions: Cat. [Ir] (0.02 mmol), alcohol (1 mmol), styrene (3 mmol), base (1.2 mmol), solvent (2 mL), 12 h, and N_2 atmosphere; the conversion was determined by GC.

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Appendix A. Supplementary material

Detailed experimental procedures, IR, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR spectra and CIF files giving crystallographic data for **2a**–**2c**. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.inoche.2014.07.033. These data include MOL files and InChiKeys of the most important compounds described in this article.

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[9] Complex **2a** was prepared via the identical employed procedure. Chloro-bridged dimer (0.10 mmol), and triphenylphosphine (0.22 mmol) were placed in a Schlenk tube containing 10 mL of CH_2Cl_2 as solvent under nitrogen atmosphere. The mixture was stirred at room temperature for 6 h. The precipitate was filtered off, and solvent was then removed in vacuo. The crude product was further recrystallized in CH_2Cl_2/hexane and a desired yellow crystal product **2a** was obtained (yield: 78%).