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Synthesis, Structure, and Photophysical Properties of Tributyl Phosphine Bisbenzothienyl Iridium(III) Complex and its Application on Transfer Hydrogenation of Acetophenone

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Keywords: Bisbenzothienyl; Phosphine; Iridium; Photophysical property; Catalysis

Abstract. A phosphine bisbenzothienyl iridium(III) complex was synthesized and characterized by IR and ^{1}H NMR spectroscopy as well as X-ray diffraction methods. The TG data suggests that the complex has an excellent thermal stability than that with an amidate ancillary ligand. Photophysical properties showed that the complex emits typical green emission.

1 Introduction

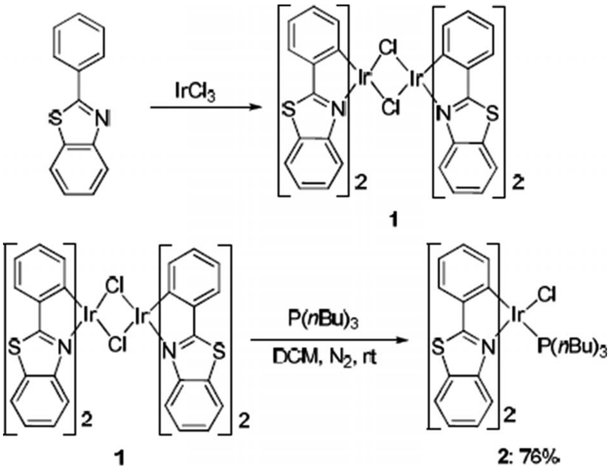
Great efforts have been made over the past decades toward developments in the design and synthesis of cyclometalated iridium(III) complexes, owing to their potential application in the field of new material,[1] such as luminescent biological labels, photoelectrochemical solar cells, electrogenerated chemiluminescence and organic light-emitting diodes (OLEDs).[2] Generally, there are two kinds of cyclometalated iridium complexes: neutral complexes such as homoleptic Ir(C N)$_3$ and heteroleptic (C N)$_2$Ir(L*X*) complexes, and cationic complexes such as [Ir(C N)$_2$(N N)]$^+$. Both neutral and ionic Ir-based complexes have the photophysical properties.[3] Neutral Ir-based complexes have been used in OLED structures, given the good chemical and photochemical stability they provide. Cationic Ir complexes have been used in light-emitting electrochemical cells (LEC), which typically consist of a single active layer, which is responsible for both carrier transport and light emission,[4] but ionic complexes may provide better catalytic reactivity.[5]

Our research in developing amides as ancillary ligand to adjust transition-metal reactivity and photophysical properties has led to the recent discovery of four-member cyclometalated Ir^{III} complexes.[6] To date, a series of amide iridium complexes and enhanced photophysical properties has been reported.[7] However, the emission spectrum is only around the green region and the thermal stability of these amide auxiliary ligands four-member cyclometalated compounds is not good, and they also have no catalytic activity.[6a] As a continuing work to synthesis of phosphine iridium(III) complex,[7] herein we report the synthesis, characterization, structure, and photophysical properties of the tributylphosphine bisbenzothienyl (bt) iridium(III) complex and its catalytic activity attemption on transfer hydrogenation of acetophenone.

2 Results and Discussion

2.1 Synthesis and Characterization

Chloro-bridged dimer [{(bt)$_2$Ir(μ-Cl)}$_2$] (**1**) and tributylphosphine were placed together in a Schlenk tube containing CH$_2$Cl$_2$ as solvent under nitrogen atmosphere.[8] The mixture was stirred at room temperature for 6 h and thus resulted in the desired complex **2** with 76 % yield (Scheme 1).



Scheme 1. The synthesis of complex **2**.

Crystal Structure of 2

The crystal structure of complex **2** was determined through X-ray crystallography. Single-crystal analysis has revealed that

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compound **2** belongs to the $P2_1/c$ space group. In the molecular structure of compound **2**, the Ir(1) atom is coordinated to one tributylphosphine, one chlorine atom, and two bt ligands all in bidentate-chelating fashions (Figure 1). The C(1)/N(2) from the benzothiazole are coordinated to Ir(1) forming a nearly planar Ir(1)–C(1)–C(6)–C(7)-N(2) five-membered ring and the angle 79.2(3)° of C(1)–Ir(1)–N(2). The bond length of Ir(1)–P(1) [2.426(2) Å] is much shorter than that of Ir(1)–Cl(1) [2.479(2) Å] (Table 1).

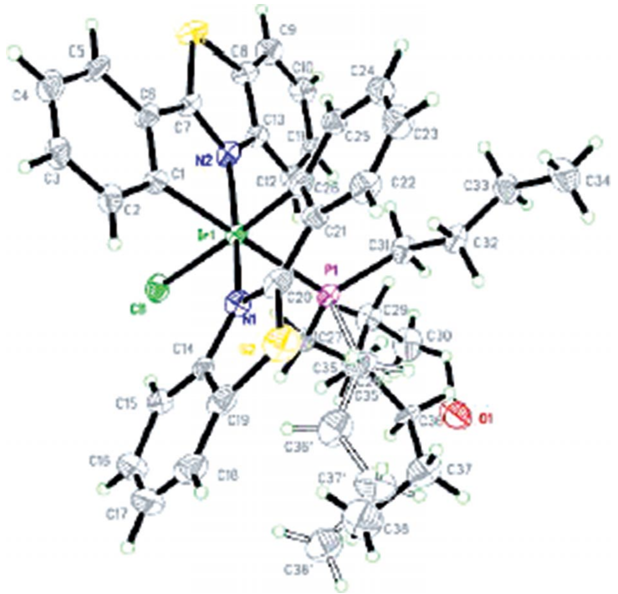


Figure 1. ORTEP diagram of complex **2** with thermal ellipsoids shown at the 30 % probability level.

Table 1. Selected bond lengths /Å and bond angles /° of complex **2**.

Bond length		Bond angle	
Ir(1)–C(26)	2.009(8)	C(26)-Ir(1)-(C1)	87.1(3)
Ir(1)–C(1)	2.064(8)	C(26)–Ir(1)–N(1)	79.7(3)
Ir(1)–N(1)	2.070(6)	C(1)–Ir(1)–N(1)	89.2(3)
Ir(1)–N(2)	2.075(7)	C(26)–Ir(1)–N(2)	91.9(3)
Ir(1)–P(1)	2.426(2)	C(1)–Ir(1)–N(2)	79.2(3)
Ir(1)–Cl(1)	2.479(2)	N(1)–Ir(1)–N(2)	166.1(3)
		C(26)–Ir(1)–P(1)	90.9(2)
		C(1)–Ir(1)–P(1)	177.2(2)
		N(1)–Ir(1)–P(1)	88.61(19)
		N(2)–Ir(1)–P(1)	102.77(19)
		C(26)–Ir(1)–Cl(1)	177.0(2)
		C(1)–Ir(1)–Cl(1)	90.7(2)
		N(1)–Ir(1)–Cl(1)	102.2(2)
		N(2)–Ir(1)–Cl(1)	85.7(2)
		P(1)–Ir(1)–Cl(1)	91.40(7)
		C(2)–C(1)–Ir(1)	130.4(7)
		C(6)–C(1)–Ir(1)	113.6(6)

2.2 Thermal Property

Furthermore, a TG experiment was investigated and the thermal curve was as shown in Figure 2. The experiment shows that this phosphine-assisted iridium(III) complex incurred a weight loss of approximately 10 % at 350 °C, but a weight loss of 60 % at 390 °C. Such data suggests that the Ir^{III} complex has much better thermal stability than that with an amidate ancillary ligand.[6]

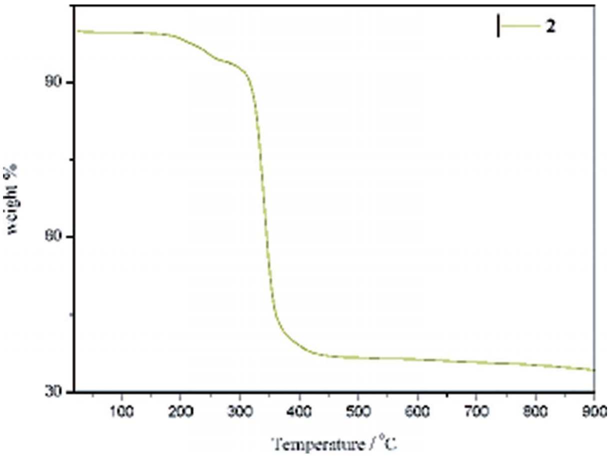


Figure 2. Thermogravimetric curves of complex **2**.

2.3 Photophysical Characterization

Additionally, the photophysical characterizations of the new-type bisbenzothienyl iridium(III) complex were tested. The results are shown in Figure 3. The absorption spectrum displays bands in the UV at 320 nm, being dramatically different from those of Ir^{III} complexes with amides as auxiliary ligands, which might be caused by different cloud density of phosphine substituent group with amides. The coordination ability of phosphine ligand usually is much stronger than that of amides.[6b] One of our research is focused on the development of color tuning function through changing ligands. Here, when phosphine groups were introduced into Ir complexes, to our delight, the wavelength of solution photoluminescence (PL) of the complex was observed around 555 nm, thus falling into the green light region. This provides us a possible method to turn our attention to the synthesis of new iridium(III) complex with phosphine ligands instead of amidate ligands.

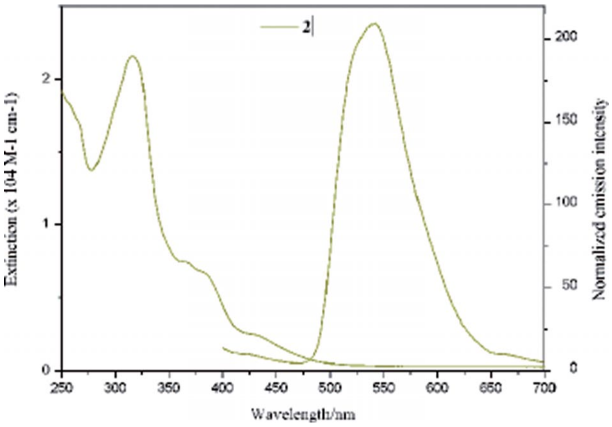
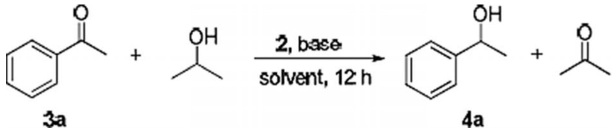


Figure 3. UV/Vis absorption and normalized PL emission spectra of Ir^{III} complex **2**.

2.4 Catalytic Activity

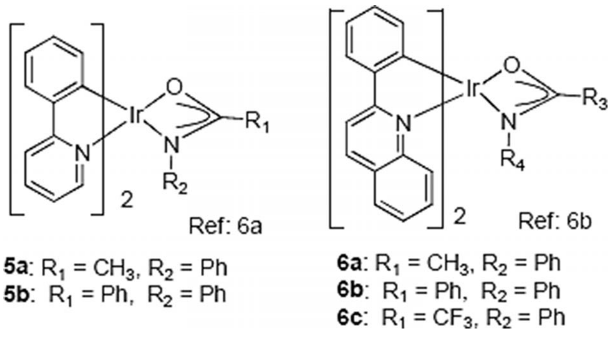
Next, we sought to expand its catalytic activity in the transfer hydrogenation reaction, so the classical acetophenone with 2-propanol was chosen as the model substrates for reaction examination. The effects of base, solvent, and temperature were all checked for the purpose of a better yield, the results of which are shown in Table 2. We found that the best reaction conditions could be summarized as follows: 2 mol-% of **2** catalyst, 1.5 equivalent of *t*BuOK, toluene as the reaction solvent, at 110 °C (Table 2, entry 5), and in this conditions, the product (**4a**) was checked with 65 % conversion. The comparison to catalytic activity of reported amide iridium complexes[6] was also conducted. The results showed that these amide iridium complexes had nearly no catalytic reactivity (Table 2, entries 8–12 and Scheme 2).

Table 2. Transfer hydrogenation of acetophenone with 2-propanol by bisbenzothienyl iridium(III) complex **2** [a].



Entry	Base	Solvent	Temp. /°C	Conv. /%
1	none	Toluene	110	24
1	K_2CO_3	Toluene	110	37
2	K_2CO_3	DMF	110	24
3	K_2CO_3	DMSO	110	25
4	KOH	Toluene	110	49
5	*t*BuOK	Toluene	110	65
6	*t*BuOK	Toluene	90	38
7	*t*BuOK	Toluene	130	57
8	*t*BuOK	Toluene	110 [b]	<5
9	*t*BuOK	Toluene	110 [c]	<5
10	*t*BuOK	Toluene	110 [d]	<5
11	*t*BuOK	Toluene	110 [e]	<5
12	*t*BuOK	Toluene	110 [f]	<5

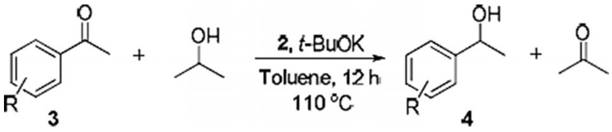
a) Reaction conditions: Cat. **2** (0.02 mmol), acetophenone (1 mmol), 2-propanol (20 mmol), base (1.5 mmol), solvent (2 mL), 12 h, N_2 atmosphere, the conversion was determined by GC. b) Catalyst **5a** was used. c) Catalyst **5b** was used. d) Catalyst **6a** was used. e) Catalyst **6b** was used. f) Catalyst **6c** was used.

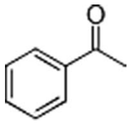
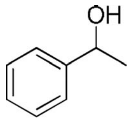
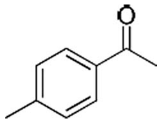
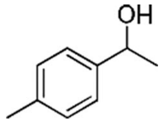
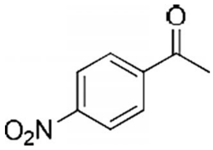
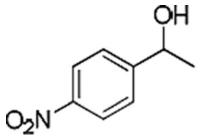
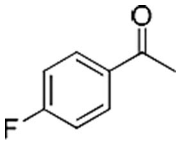
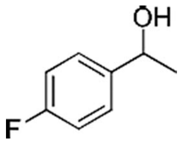
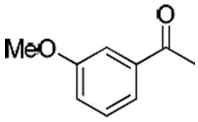
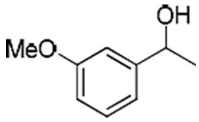
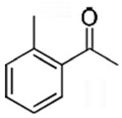
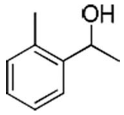


Scheme 2. Several pyridyl- and quinolyl-substituted iridium(III) complexes.

Under the best reaction conditions, the substrate scope was also explored (Table 3). In general, all the desired products were obtained with moderate yields. The best yield was achieved in 68 % yield (entry 6, Table 3). Although the yield is not good, the introducing phosphine ligand gives us a possible method to enhance catalytic activity about iridium-catalyzed reactions.

Table 3. Transfer hydrogenation of ketones with 2-propanol by catalyst **2** [a].



Entry	Alcohol	Product	Yield /%
1			**4a** (65)
2			**4b** (61)
3			**4c** (47)
4			**4d** (54)
5			**4e** (63)
6			**4f** (68)

a) Reaction conditions: Cat. **2** (0.02 mmol), ketone **3** (1 mmol), 2-propanol (20 mmol), *t*BuOK (1.5 mmol), toluene (2 mL), 12 h, N_2 atmosphere, 110 °C, the yields were determined by GC.

3 Conclusions

A benzothienyl skeleton tributyl phosphine iridium(III) complex (**2**) was synthesized and characterized through X-ray crystallography. The TG data suggests that the complex showed a weight loss of approximately 10 % at 350 °C, and has much better thermal stability than that with an amidate ancillary ligand. Photophysical properties showed that complex **2** gave the typical green emission. Moreover, the iridium complex could be applied on the transfer hydrogenation reaction of acetophenone and 2-propanol with moderate yield. Compared to amide iridium complexes, the enhanced catalytic activity of phosphine iridium complex provides us a possible method toward iridium-catalyzed reactions.

4 Experimental Section

4.1 Materials

$IrCl_3 \cdot 3H_2O$ and other chemicals were obtained from commercial resource and used without further purification. Chloro-bridged dimer $(bt)_2Ir(\mu\text{-}Cl)_2Ir(bt)_2$ (**1**) was prepared according to the reported literature.[8a] All solvents were dried by standard methods.

4.2 General Experiments

All of the reactions dealing with air and/or moisture-sensitive reactions were carried out in an atmosphere of nitrogen using a standard Schlenk tube. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^1H NMR, and ^{13}C NMR spectra were recorded with Varian 400 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ = 0.00 ppm), $CDCl_3$ (δ = 7.26 ppm) for ^1H NMR and $CDCl_3$ (δ = 77.23 ppm) for ^{13}C NMR spectroscopy.

4.3 Synthesis and Characterization Data of Complex 2

A mixture of $[\{(bt)_2Ir(\mu\text{-}Cl)\}_2]$ (0.10 mmol) and tributylphosphine (0.22 mmol) were placed together in a Schlenk tube containing CH_2Cl_2 as solvent in a nitrogen atmosphere. The resulting mixture was stirred at room temperature for 6 h. After removal of solvents, the crude product was further recrystallized from CH_2Cl_2/hexane to give the desired product **2** (yield: 76 %). **IR** (KBr): $\tilde{\nu}$ = 3056 m, 2956 s, 2929 m, 2869 s, 1581 s, 1468 s, 1448 s, 1437 s, 1407 s, 1296 m, 1265 m, 1251 m, 1159 w, 1093 w, 1024 m, 997 m, 754 s, 732 s, 723 s cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.86 (d, J = 8.3 Hz, 1H), 7.96–7.85 (m, 2H), 7.81 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 7.5 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.56–7.50 (m, 2H), 7.46 (dd, J = 12.9, 5.3 Hz, 2H), 6.91–6.81(m, 2H), 6.71 (t, J = 7.4 Hz, 1H), 6.67–6.62 (m, 2H), 6.10 (dd, J = 7.1, 5.1 Hz, 1H), 1.88–1.75 (m, 3H), 1.72–1.61 (m, 3H), 1.06–0.86 (m, 12H), 0.62 (t, J = 7.0 Hz, 9H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 183.64 (d, J = 8.4 Hz), 179.30, 163.79, 162.78, 152.30, 149.71, 147.85 (d, J = 5.6 Hz), 141.24, 140.10, 133.70, 131.69, 131.29, 131.28–130.59(m), 127.57, 126.04–124.58 (m), 125.22, 124.73, 123.26, 122.70, 121.79, 120.92 (d, J = 4.0 Hz), 65.84, 26.23 (d, J = 4.7 Hz), 24.12–23.70 (m), 24.02, 23.80, 13.39 ppm. **^{31}P NMR** (162 MHz, $CDCl_3$): δ = –28.33 ppm. $C_{38}H_{43}ClIrN_2PS_2$: C 53.66; H 5.10, N 3.29 %. found: C 53.49; H 5.23, N 3.18 %.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-980976 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Acknowledgements

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