ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Mechanistic Investigation of Improved Syntheses of Iridium(III)-Based OLED Phosphors

Cheng-Huei Lin,[†] Yuan-Chieh Chiu,[†] Yun Chi,*[,†] Yu-Tai Tao,*[,‡] Liang-Sheng Liao,*[,§] Meu-Rurng Tseng,[∥] and Gene-Hsiang Lee[⊥]

[†]Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan

[‡]Institute of Chemistry, Academia Sinica, Taipei 11529, Taiwan

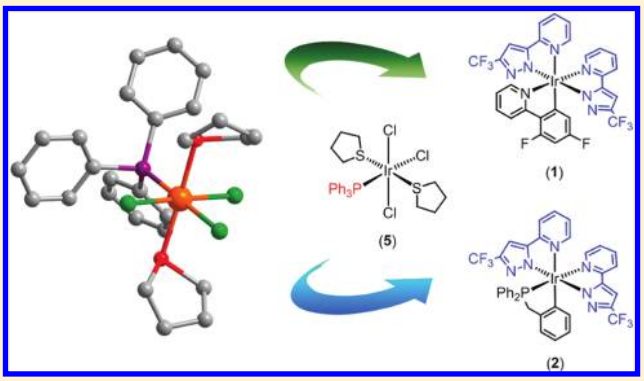
[§]Institute of Functional Nano & Soft Materials, SooChow University, Suzhou 215123, People's Republic of China

[∥]Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsinchu 31040, Taiwan

[⊥]Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan

Supporting Information

ABSTRACT: Treatment of $[IrCl_3(tht)_3]$ (tht = tetrahydrothiophene) with a stoichiometric amount of PPh_3 gave the monosubstitution product $[Ir(tht)_2(PPh_3)Cl_3]$ (**5**), whose synthesis, particularly that leading to the effective preparation of OLED phosphors, was studied and optimized to achieve the best product yields. Thus, the independent treatment of **5** with 2,4-difluorophenylpyridine (dfppyH) or with variable amounts of benzyldiphenylphosphine (bdpH) gave rise to the formation of the cyclometalation products $[Ir(dfppy)(tht)(PPh_3)Cl_2]$ (**7**), $[Ir(bdp)(bdpH)(tht)Cl_2]$ (**8**), and $[Ir(bdp)(PPh_3)(tht)Cl_2]$ (**10**), depending on the stoichiometry and conditions employed. Upon further treatment with 5-pyridyl-3-trifluoromethyl-1*H*-pyrazole (fppzH), these Ir(III) complexes **7**, **8**, and **10** were capable of yielding the phosphors $[Ir(dfppy)(fppz)_2]$ (**1**), $[Ir(bdp)_2(fppz)]$ (**4**), and $[Ir(bdp)(fppz)_2]$ (**2**), respectively. The general mechanism en route to their formation was studied and discussed.



1. INTRODUCTION

Luminescent Ir(III) metal complexes, particularly those with chelating cyclometalates, play a key role in the recent development of optoelectronic technologies such as organic light-emitting diodes (OLEDs),[1−9] light-emitting electrochemical cells,[10] biological labels,[11−13] chemical sensors,[14,15] and solid-state organic lighting applications.[16] The attraction of these complexes comes from their higher chemical stability due to strong metal−ligand bonding interactions, as well as their longer excitation lifetimes and higher emission quantum yields.[17] Furthermore, the strong spin−orbit coupling induced by the central Ir(III) metal ion promotes an efficient intersystem crossing from the singlet to the triplet excited state manifold, which then facilitates strong electroluminescence by harnessing both singlet and triplet excitons of the as-fabricated optoelectronic devices.[18−20] As a result, syntheses of Ir(III) complexes have been extensively examined in the past two decades.[21−23]

Conventionally, the syntheses are achieved with the employment of three distinctive iridium source reagents: i.e. $IrCl_3{\cdot}nH_2O$, $Ir(acac)_3$, and $[Ir(COD)(\mu\text{-}Cl)]_2$. It has been reported that the nitrogen-containing heteroaromatics (C∧N)H can readily react with $IrCl_3{\cdot}nH_2O$ in high-boiling protic solvents to afford a dicyclometalated dimer of the formula $[(C\wedge N)_2Ir(\mu\text{-}Cl)]_2$.[24] Subsequent treatment of this class of intermediates with any potentially anionic chelate (L∧X)H affords the heteroleptic $[(C\wedge N)_2Ir(L\wedge X)]$ in high yields (eqs 1 and 2).[25]

$$IrCl_3{\cdot}nH_2O + (C\wedge N)H\ (2\ \text{equiv}) \rightarrow [(C\wedge N)_2Ir(\mu\text{-}Cl)]_2 \quad (1)$$

$$[(C\wedge N)_2Ir(\mu\text{-}Cl)]_2 + (L\wedge X)H \rightarrow [(C\wedge N)_2Ir(L\wedge X)] \quad (2)$$

$$Ir(acac)_3 + (C\wedge N)H\ (3\ \text{equiv}) \rightarrow [Ir(C\wedge N)_3] \quad (3)$$

Alternatively, the tris-substituted cyclometalate complexes $[Ir(C\wedge N)_3]$ can be obtained from either treatment of the aforementioned $[(C\wedge N)_2Ir(\mu\text{-}Cl)]_2$ with more (C∧N)H chelate[26] or by simply heating $Ir(acac)_3$ (acacH = acetylacetone) with 3 equiv of (C∧N)H at high temperature (eq 3).[27,28] The disadvantage of the $Ir(acac)_3$ reagent is its lower synthetic yield from $IrCl_3{\cdot}nH_2O$, which then raises the cost for acquiring this starting material. Third, the COD reagent $[Ir(COD)(\mu\text{-}Cl)]_2$ (COD = 1,4-cyclooctadiene), due to its +1 formal

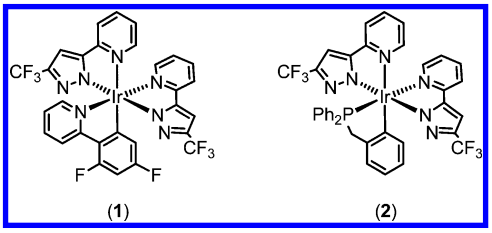
Received: April 19, 2012
Published: May 25, 2012

oxidation state and greater tendency to form strong bonds with carbon-based σ-donors, was reported to be particularly useful for synthesizing cyclometalated Ir(III) complexes that possess a five-membered N-heterocyclic carbene framework.[29,30] Additionally, a more recent development was the preparation of tris-heteroleptic complexes, for which employment of $[Ir(COD)(\mu\text{-}Cl)]_2$ allowed the isolation of [(ppy)(dfppy)Ir(acac)] (ppyH = 2-phenylpyridine and dfppyH = 2,4-difluorophenylpyridine) in good yield over two steps (eqs 4 and 5), giving a significant improvement over methods that use $IrCl_3 \cdot nH_2O$ as the starting material.[31]

$$[Ir(COD)(\mu\text{-}Cl)]_2 + ppyH + dfppyH \rightarrow [(ppy)(dfppy)Ir(\mu\text{-}Cl)]_2 \quad (4)$$

$$[(ppy)(dfppy)Ir(\mu\text{-}Cl)]_2 + acacNa \rightarrow [(ppy)(dfppy)Ir(acac)] \quad (5)$$

Recently, a fourth reagent, $IrCl_3(tht)_3$ (tht = tetrahydrothiophene) has been employed in synthesizing a class of true blue emitting Ir(III) complexes such as $[Ir(dfppy)(fppz)_2]$ (**1**; fppzH = 3-trifluoromethyl-5-(2-pyridyl)pyrazole), from which an OLED with maximum external quantum efficiency (EQE) of 8.5% and CIE(x,y) coordinates of 0.16 and 0.18 was obtained.[32] Unfortunately, the reported reaction affords the desired isomeric Ir(III) complexes only in lower yield (≤20%). Herein, we describe a new methodology which allowed better control of the stereochemistry and afforded the desired product in higher yields. Moreover, the same strategy was equally applicable for the scale-up preparation of the true blue phosphor $[Ir(bdp)(fppz)_2]$ (**2**; bdpH = benzyldiphenylphosphine) and functional derivatives that have shown a maximum EQE of up to 11.7% and CIE(x,y) coordinates of 0.16 and 0.11.[33] For both synthetic reactions, key intermediates en route to the desired products were characterized by NMR spectroscopy and single-crystal X-ray diffraction methods. Apparently, the present investigation is valuable for the efficient synthesis of relevant Ir(III) phosphors that cannot be prepared by traditional methods.



2. EXPERIMENTAL SECTION

General Procedures. All reactions were performed under an argon atmosphere, and solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored using precoated TLC plates (0.20 mm with fluorescent indicator UV254). Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) or fast atom bombardment (FAB) mode. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury-400 or an INOVA-500 instrument. Elemental analysis was carried out with a Heraeus CHN-O Rapid elemental analyzer. The Ir(III) metal reagent $[IrCl_3(tht)_3]$ was synthesized using the literature method.[34]

Preparation of $[Ir(tht)_2(PPh_3)Cl_3]$ (5). A mixture of $IrCl_3(tht)_3$ (500 mg, 0.89 mmol) and triphenylphosphine (PPh_3, 256 mg, 1.0 mmol) in decalin (15 mL) was heated to reflux for 2 h. After the reaction mixture was cooled to room temperature, the solvent was removed under vacuum and the residue was dissolved in CH_2Cl_2 and then filtered through a pad of Celite. The filtrate was collected and concentrated on a rotavap to give a crude product. Further crystallization from a mixture of CH_2Cl_2 and hexane at room temperature gave yellow crystals (594 mg, 0.81 mmol, 91%). Single crystals of **5** were obtained from a mixture of ethyl acetate and hexane at room temperature.

*Spectral Data of **5**:* MS (FAB, ^{193}Ir) m/z 702 (M − Cl)$^+$; ^{1}H NMR (400 MHz, $CDCl_3$, 294 K) δ 7.80−7.71 (m, 6H), 7.42−7.32 (m, 9H), 3.80−3.69 (m, 4H), 2.63−2.52 (m, 4H), 2.38−2.22 (m, 4H), 1.98−1.86 (m, 4H); ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, 294 K) δ −21.5 (s, 1P). Anal. Calcd for $C_{26}H_{31}Cl_3IrPS_2$: C, 42.36; H, 4.24. Found: C, 42.42; H, 4.39.

*Selected Crystal Data of **5**:* $C_{27.50}H_{34.50}Cl_3IrO_{1.50}PS_2$; M_r = 782.69; monoclinic; space group $P2_1/c$; a = 13.1972(7) Å, b = 10.2905(5) Å, c = 21.7022(11) Å, β = 95.0332(11)°, V = 2935.9(3) Å^3; Z = 4; ρ_{calcd} = 1.771 Mg m^{-3}; F(000) = 1546; crystal size 0.38 × 0.33 × 0.05 mm^3; λ(Mo Kα) = 0.710 73 Å; T = 150(2) K; μ = 5.040 mm^{-1}; 20 309 reflections collected, 6741 independent reflections (R_{int} = 0.0431), GOF = 1.029, final R1($I > 2\sigma(I)$) = 0.0289 and wR2(all data) = 0.0742.

Preparation of $[Ir(tht)(PPh_3)_2Cl_3]$ (6). *Method 1.* A mixture of $IrCl_3(tht)_3$ (400 mg, 0.71 mmol) and PPh_3 (392 mg, 1.5 mmol) in decalin (15 mL) was heated to reflux for 6 h. After the reaction mixture was cooled to room temperature, the solvent was removed under vacuum and the solid residue was triturated with hexane (50 mL) and collected by filtration. Further purification was done by washing with CH_2Cl_2 to give a yellow powder (396 mg, 0.44 mmol, 61%).

Method 2. A procedure similar to that described for method 1 was conducted. A mixture of **5** (100 mg, 0.136 mmol) and PPh_3 (39 mg, 0.15 mmol) in decalin (10 mL) was heated to reflux for 0.5 h. Complex **6** was obtained in 24% yield (29 mg, 0.032 mmol).

*Spectral Data of **6**:* MS (FAB, ^{193}Ir) m/z 787 [M − (tht, Cl)]$^+$; ^{1}H NMR (400 MHz, $CDCl_3$, 294 K) δ 7.64 (t, J = 9.0 Hz, 6H), 7.52 (t, J = 9.0 Hz, 6H), 7.36−7.20 (m, 5H), 7.20−7.08 (m, 13H), 3.65 (br, 2H), 2.33 (br, 2H), 2.20 (br, 2H), 1.85 (br, 2H); ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, 294 K) δ −25.4 (d, J_{PP} = 13.5 Hz, 1P), −30.0 (d, J_{PP} = 13.5 Hz, 1P). Anal. Calcd for $C_{40}H_{38}Cl_3IrP_2S$: C, 52.72; H, 4.20. Found: C, 52.09; H, 4.20.

Preparation of $[Ir(dfppy)(tht)(PPh_3)Cl_2]$ (7). *Method 1.* A mixture of **5** (154 mg, 0.21 mmol) and dfppyH (44 mg, 0.23 mmol) in decalin (10 mL) was heated to reflux for 1 h. After evaporation of solvent, the residue was dissolved in CH_2Cl_2 and the solution was then filtered through a pad of Celite. The filtrate was concentrated on a rotavap, followed by crystallization from a mixture of CH_2Cl_2 and hexane at room temperature, giving pale yellow crystals (31 mg, 0.039 mmol, 19%).

Method 2. A mixture of $IrCl_3(tht)_3$ (100 mg, 0.18 mmol), dfppyH (37 mg, 0.20 mmol), and PPh_3 (49 mg, 0.187 mmol) in decalin (8 mL) was heated to reflux for 1.5 h. After the reaction mixture was cooled to room temperature, the solution was concentrated, the residue was dissolved in CH_2Cl_2, and this solution was then filtered through a pad of Celite. After concentration and recrystallization, complex 7 was obtained in 39% yield (55 mg, 0.068 mmol).

*Spectral Data of **7**:* MS (FAB, ^{193}Ir) m/z 804 (M + 1)$^+$; ^{1}H NMR (400 MHz, $CDCl_3$, 294 K) δ 9.16 (d, J = 4.8 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.51−7.40 (m 7H), 7.30−7.16 (m, 3H), 7.15−7.05 (m, 7H), 6.63 (t, J = 6.6 Hz, 1H), 6.45−6.35 (m, 1H), 3.59 (br, 1H), 2.77 (br, 1H), 2.64 (br, 1H), 2.01 (br, 3H), 1.82 (br, 1H), 1.70 (br, 1H); ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$, 294 K) δ −107.1 (m, 1F), −111.9 (t, J = 10.8 Hz, 1F); ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, 294 K) δ −15.8 (s, 1P). Anal. Calcd for $C_{33}H_{29}Cl_2F_2IrNPS$: N, 1.74; C, 49.31; H, 3.64. Found: N, 2.23; C, 48.62; H, 3.90.

*Selected Crystal Data of **7**:* $C_{33}H_{29}Cl_2F_2IrNPS$; M_r = 803.70; orthorhombic; space group $P2_12_12_1$; a = 10.6610(8) Å, b =

13.0231(10) Å, c = 21.6671(16) Å, V = 3008.2(4) Å^3; Z = 4; ρ_{calcd} = 1.775 Mg m^{-3}; $F(000)$ = 1576; crystal size 0.25 × 0.25 × 0.20 mm^3; λ(Mo Kα) = 0.710 73 Å; T = 150(2) K; μ = 4.776 mm^{-1}; 17 246 reflections collected, 6851 independent reflections (R_{int} = 0.0524), GOF = 1.043, final R1($I > 2\sigma(I)$) = 0.0671 and wR2(all data) = 0.1580.

Preparation of [Ir(dfppy)(fppz)$_2$] (1). *Method 1.* A mixture of **7** (151 mg, 0.19 mmol), 5-pyridyl-3-trifluoromethyl-1*H*-pyrazole (fppzH, 87 mg, 0.41 mmol), and Na_2CO_3 (100 mg, 0.94 mmol) in decalin (8 mL) was heated to reflux for 12 h. After the reaction mixture was cooled to room temperature, the solvent was removed and the residue was purified by silica gel column chromatography using a 2/1 mixture of ethyl acetate and hexane as the eluent. Further crystallization from a mixture of CH_2Cl_2 and hexane at room temperature gave pale yellow crystals of **1** (83 mg, 0.10 mmol, 55%).

Method 2. A mixture of $IrCl_3(tht)_3$ (150 mg, 0.27 mmol), PPh_3 (73 mg, 0.28 mmol), and dfppyH (54 mg, 0.28 mmol) in decalin (15 mL) was heated at 190 °C for 6 h. After the reaction mixture was cooled to room temperature, fppzH (120 mg, 0.56 mmol) and Na_2CO_3 (142 mg, 1.3 mmol) were added and the mixture was heated to reflux for another 24 h. After chromatographic separation and recrystallization, complex **1** was obtained in 32% yield (69 mg, 0.086 mmol).

*Spectral Data of **1**:* MS (FAB, ^{192}Ir) m/z 808 (M + 1)$^+$; ^{1}H NMR (400 MHz, d_6-acetone, 294 K) δ 8.26 (d, J_{HH} = 8.8 Hz, 1H), 8.18–8.03 (m, 4H), 7.94–7.90 (m, 2H), 7.44–7.39 (m, 3H), 7.32 (td, J_{HH} = 5.6, 1.6 Hz, 1H), 7.23 (s, 1H), 7.21 (s, 1H), 7.16 (td, J_{HH} = 6.2, 1.2 Hz, 1H), 6.63 (td, J_{HH} = 8.2, 2.4 Hz, 1H), 5.82 (dd, J_{HH} = 8.8, 2.4 Hz, 1H); ^{19}F NMR (470 MHz, d_6-acetone, 294 K) δ −111.8 (s, 1F), −109.6 (s, 1F), −60.7 (s, 3F), −60.6 (s, 3F). Anal. Calcd for $C_{29}H_{16}F_8IrN_7$: N, 12.15; C, 43.18; H, 2.00. Found: N, 12.03; C, 43.35; H, 2.02.

Preparation of [Ir(bdp)(bdpH)(tht)Cl$_2$] (8). *Method 1.* A mixture of **5** (100 mg, 0.14 mmol) and bdpH (81 mg, 0.29 mmol) in decalin (6 mL) was heated to reflux for 1 h. After the reaction mixture was cooled to room temperature, the solvent was removed under vacuum and the residue was filtered through a pad of Celite. The filtrate was collected and concentrated on a rotavap to give a crude product. Crystallization from a mixture of CH_2Cl_2 and hexane at room temperature gave pale yellow crystals (92 mg, 0.10 mmol, 75%).

Method 2. A mixture of $IrCl_3(tht)_3$ (200 mg, 0.36 mmol), bdpH (206 mg, 0.75 mmol), and PPh_3 (98 mg, 0.37 mmol) in decalin (10 mL) was heated to reflux for 12 h. After the mixture was cooled to room temperature, the solvent was removed under vacuum and the residue was dissolved in CH_2Cl_2 and filtered through a pad of Celite. After concentration and recrystallization, complex **8** was obtained in 61% yield (195 mg, 0.22 mmol).

*Spectral Data of **8**:* MS (FAB, ^{193}Ir) m/z 868 (M − Cl)$^+$; ^{1}H NMR (500 MHz, CD_2Cl_2, 233 K) δ 8.81 (br, 1H), 8.03 (d, J = 7.5 Hz, 1H), 7.71 (br, 2H), 7.39–7.29 (m, 4H), 7.29–7.19 (m, 4H), 7.19–7.11 (m, 4H), 7.09 (t, J = 6.5 Hz, 2H), 7.01 (t, J = 7.5 Hz, 1H), 6.95 (t, J = 7.5 Hz, 1H), 6.79 (t, J = 7.5 Hz, 1H), 6.78–6.71 (m, 2H), 6.65 (t, J = 7.5 Hz, 2H), 6.34 (t, J = 9.0 Hz, 2H), 6.05 (d, J = 7.5 Hz, 2H), 4.79 (dd, J = 15.0, 10.0 Hz, 1H), 3.79–3.69 (m, 1H), 3.63 (dd, J = 15.0, 10.0 Hz, 1H), 3.51 (dd, J = 17.5, 11.5 Hz, 1H), 3.10–3.02 (m, 1H), 2.01–1.91 (m, 2H), 1.86 (dd, J = 17.5, 11.5 Hz, 1H), 1.72–1.56 (m, 4H); ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 233 K) δ 4.63 (d, J_{PP} = 16.2 Hz, 1P), −14.8 (d, J_{PP} = 16.2 Hz, 1P). Anal. Calcd for $C_{42}H_{41}Cl_2IrP_2S$: C, 55.87; H, 4.58. Found: C, 55.84; H, 4.64.

*Selected Crystal Data of **8**:* $C_{84}H_{82}Cl_4Ir_2P_4S_2$; M_r = 1805.70; monoclinic; space group $C2/c$; a = 43.3581(17) Å, b = 8.8949(3) Å, c = 19.2344(7) Å, β = 103.151(2)°, V = 7223.5(5) Å^3; Z = 4; ρ_{calcd} = 1.660 Mg m^{-3}; $F(000)$ = 3600; crystal size 0.28 × 0.25 × 0.25 mm^3; λ(Mo Kα) = 0.710 73 Å; T = 150(2) K; μ = 4.022 mm^{-1}; 27 074 reflections collected, 8308 independent reflections (R_{int} = 0.0318), GOF = 1.120, final R1($I > 2\sigma(I)$) = 0.0245 and wR2(all data) = 0.0625.

Preparation of [Ir(bdp)(bdpH)(fppz)Cl] (9). *Method 1.* A mixture of **8** (100 mg, 0.12 mmol), fppzH (26 mg, 0.12), and Na_2CO_3 (58 mg, 0.55 mmol) in decalin (8 mL) was heated for 0.5 h at 160 °C. After the mixture was cooled to room temperature, the solvent was removed under vacuum and the residue was filtered through a pad of Celite. The filtrate was collected and concentrated on a rotavap to give a crude product. Crystallization from CH_2Cl_2 and hexane at room temperature gave yellow crystals of **9** (62 mg, 0.063 mmol, 56%).

Method 2. A mixture of $IrCl_3{\cdot}3H_2O$ (106 mg, 0.30 mmol) and bdpH (170 mg, 0.62 mmol) in degassed 2-methoxyethanol (15 mL) was heated at 120 °C for 12 h. After the mixture was cooled to room temperature, fppzH (64 mg, 0.30 mmol) and Na_2CO_3 (320 mg, 3.0 mmol) were added and the mixture was stirred at room temperature for 3 h. An excess of water was added to induce precipitation, which was collected by filtration and washed with methanol and ether in sequence. The residue was purified by silica gel column chromatography using CH_2Cl_2 as the eluent. Further crystallization from CH_2Cl_2 and hexane at room temperature gave yellow crystals of **9** (120 mg, 0.12 mmol, 40%). Single crystals suitable for an X-ray diffraction study were obtained from a mixture of CH_2Cl_2 and hexane at room temperature.

*Spectral Data of **9**:* MS (FAB, ^{193}Ir) m/z 992 (M + 1)$^+$, 956 (M − Cl$^+$); ^{1}H NMR (500 MHz, $CDCl_3$, 294 K) δ 8.26 (d, J = 7.0 Hz, 1H), 7.65 (t, J = 9.0 Hz, 2H), 7.43 (t, J = 9.0 Hz, 1H), 7.37–7.30 (m, 3H), 7.21 (d, J = 7.0 Hz, 1H), 7.16–7.08 (m, 5H), 7.06 (d, J = 7.0 Hz, 1H), 7.04 (d, J = 7.0 Hz, 1H), 7.02 (s, 1H), 7.00–6.90 (m, 3H), 6.84 (t, J = 7.5 Hz, 2H), 6.82–6.77 (m, 4H), 6.68 (t, J = 7.5 Hz, 2H), 6.63 (t, J = 7.5 Hz, 2H), 6.42–6.35 (m, 5H), 4.98 (dd, J = 15.0, 10.0 Hz, 1H), 4.28 (dd, J = 15.0, 10.0 Hz, 1H), 3.73 (dd, J = 16.5, 10.0 Hz, 1H), 3.02 (dd, J = 16.5, 10.0 Hz, 1H); ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$, 294 K) δ −60.33 (s, 3F); ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, 294 K) δ 2.70 (d, J = 16.5 Hz, 1P), −17.33 (d, J = 16.5 Hz, 1P). Anal. Calcd for $C_{47}H_{38}ClF_3IrN_3P_2$: N, 4.24; C, 56.94; H, 3.86. Found: N, 4.23; C, 56.77; H, 4.16.

*Selected Crystal Data of **9**:* $C_{47}H_{38}ClF_3IrN_3P_2$; M_r = 991.39; monoclinic; space group $P2_1/n$; a = 12.4793(4) Å, b = 20.8875(7) Å, c = 15.9283(5) Å, β = 109.143(1)°, V = 3922.3(2) Å^3; Z = 4; ρ_{calcd} = 1.679 Mg m^{-3}; $F(000)$ = 1968; crystal size 0.36 × 0.15 × 0.12 mm^3; λ(Mo Kα) = 0.710 73 Å; T = 150(2) K; μ = 3.608 mm^{-1}; 29 888 reflections collected, 9005 independent reflections (R_{int} = 0.0444), GOF = 1.034, final R1($I > 2\sigma(I)$) = 0.0276 and wR2(all data) = 0.0595.

Preparation of [Ir(bdp)$_2$(fppz)] (4). A mixture of **9** (120 mg, 0.12 mmol) and silver trifluoromethanesulfonate (AgOTf, 40 mg, 0.16 mmol) in 2-methoxyethanol (10 mL) was heated at 120 °C for 1 h in the dark. After the mixture was cooled to room temperature, the mixture was filtered through a pad of Celite and mixed with water to induce precipitation. The collected precipitate was next purified by silica gel column chromatography using CH_2Cl_2 as the eluent. Crystallization from CH_2Cl_2 and hexane at room temperature gave white crystals (38 mg, 0.04 mmol, 33%).

Trapping of [Ir(bdp)(PPh$_3$)(tht)Cl$_2$] (10). *Method 1.* A mixture of **5** (100 mg, 0.14 mmol) and bdpH (41 mg, 0.15 mmol) in decalin (8 mL) was heated to reflux for 1 h. After the mixture was cooled to room temperature, the solvent was removed under vacuum, and hexane was added (20 mL), the resulting precipitate was collected by filtration. Further purification was done by washing with CH_2Cl_2 and hexane to give a pale yellow powder (101 mg), the major component of which was believed to be [Ir(bdp)(PPh$_3$)(tht)Cl$_2$] (**10**).

Method 2. A mixture of **6** (100 mg, 0.11 mmol) and bdpH (33 mg, 0.12 mmol) in decalin (8 mL) was heated to reflux for 2 h. A pale yellow powder (106 mg) was obtained as a mixture of products.

Preparation of [Ir(bdp)(fppz)$_2$] (2). *Method 1.* A mixture of **5** (150 mg, 0.20 mmol) and bdpH (62 mg, 0.22 mmol) in decalin (10 mL) was heated at 180 °C for 4.5 h. After the mixture was cooled to room temperature, fppzH (92 mg, 0.428 mmol) and Na_2CO_3 (108 mg, 1.02 mmol) were added and the mixture was heated to reflux for another 16 h. After cooling and evaporation of solvent, the residue was purified by silica gel column chromatography with a 1/1 mixture of ethyl acetate and hexane as eluent. Further crystallization from mixed CH_2Cl_2 and hexane at room temperature gave white crystals of **2** (63 mg, 0.071 mmol, 35%).

Method 2. A mixture of **6** (160 mg, 0.18 mmol) and bdpH (53 mg, 0.19 mmol) in decalin (10 mL) was heated at 180 °C for 3 h. After the mixture was cooled to room temperature, fppzH (79 mg, 0.37 mmol)

dx.doi.org/10.1021/om300325y | *Organometallics* 2012, 31, 4349–4355

and Na_2CO_3 (93 mg, 0.88 mmol) were added and the mixture was heated to reflux for another 16 h. After chromatographic separation and recrystallization, complex **2** was obtained in 35% yield (54 mg, 0.06 mmol).

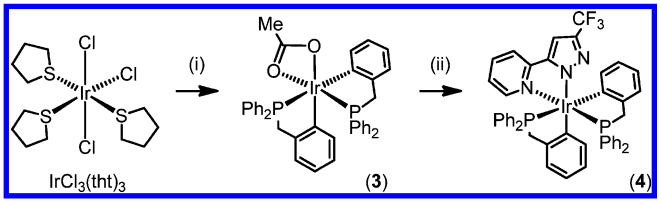
Method 3. A mixture of $IrCl_3(tht)_3$ (155 mg, 0.28 mmol), PPh_3 (78 mg, 0.30 mmol), and bdpH (83 mg, 0.301 mmol) in decalin (10 mL) was heated at 180 °C for 6 h. After the mixture was cooled to room temperature, fppzH (120 mg, 0.56 mmol) and Na_2CO_3 (150 mg, 1.4 mmol) were added and the mixture was heated to reflux for 12 h. After chromatographic separation and recrystallization, complex **2** was obtained in 44% yield (109 mg, 0.12 mmol).

Single Crystal X-ray Diffraction Studies. Single-crystal X-ray diffraction data were measured on a Bruker SMART Apex CCD diffractometer using Mo Kα radiation (λ = 0.710 73 Å). Data collection was executed using the SMART program. Cell refinement and data reduction were performed with the SAINT program. The structure was determined using the SHELXTL/PC program and refined using full-matrix least squares. Selected crystallographic data and refinement parameters are summarized in the section following their synthetic procedures and spectral data.

3. RESULTS AND DISCUSSION

Improved Synthesis of 1. In the 1960s, Chatt and coworkers reported that PEt_3 can readily coordinate to chloroiridic acid, H_2IrCl_6, in forming the stable yellow complex $[IrCl_3(PEt_3)_3]_3$, which was the first example of an Ir(III) atom accommodating up to three phosphine donors.[35] Subsequently, it was noted that, upon treatment of $IrCl_3{\cdot}nH_2O$ with dimethyl(1-naphthyl)phosphine at high temperature, the phosphine ligand underwent both metal coordination and C−H activation at the naphthyl pendant, giving a distinctive class of cyclometalated complexes.[36] Bearing these precedents in mind, we then synthesized the novel Ir(III) complex [Ir(bdp)$_2$(OAc)] (**3**) by treatment of $[Ir(tht)_3Cl_3]$ with bdpH in the presence of sodium acetate, NaOAc (Scheme 1).[37,38] The

Scheme 1. Cyclometalation of Benzyldiphenylphosphine on an Ir(III) Metal Center[a]

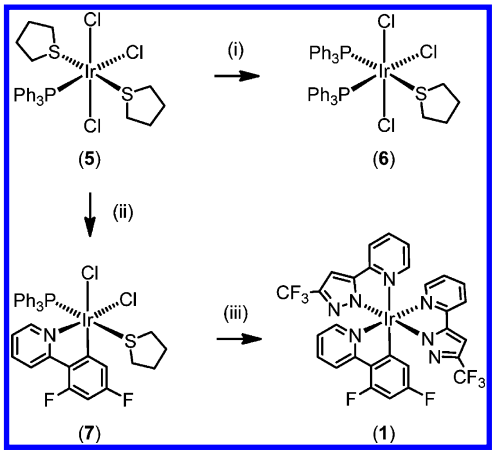


[a]Reagents and conditions: (i) bdpH, NaOAc, decalin, 196°C, 2 h; (ii) fppzH, decalin, 196 °C, 12 h.

isolation of **3** then triggered the preparation of a phosphine-containing Ir(III) phosphor; one such example is [Ir(bdp)$_2$(fppz)] (**4**), with two cyclometalated phosphorus ancillaries.

Recently, in sharp contrast to the triphenyl phosphite that yields double cyclometalation,[39,40] a bulky phosphine ligand such as PPh_3, was found to react readily with the aforementioned Ir(III) source complex $[Ir(tht)_3Cl_3]$, giving two isolable products, namely $[Ir(tht)_2(PPh_3)Cl_3]$ (**5**) and $[Ir(tht)(PPh_3)_2Cl_3]$ (**6**), in a stepwise fashion (Scheme 2). The monosubstitution product **5** was obtained as the major product for the reaction using a stoichiometric amount of PPh_3, while the disubstitution product **6** was isolated by addition of 2 equiv of PPh_3 to $[Ir(tht)_3Cl_3]$ or by treatment of the monosubstitution product **5** with a another 1 equiv of PPh_3 under similar conditions.

Scheme 2. Synthetic Procedures for the Ir(III) Metal Complex 1[a]



[a]Reagents and conditions: (i) PPh_3, decalin, 196 °C, 0.5 h; (ii) dfppyH, decalin, 196 °C, 1 h; (iii) fppzH, Na_2CO_3, decalin, 196 °C, 12 h.

In terms of purification and characterization, high-quality crystals of **5** can be easily obtained by recrystallization at room temperature; therefore, an X-ray diffraction study was used for revealing its molecular structure. In contrast, complex **6** is much less soluble in organic solvents, such that its identification is solely based on elemental analysis and multinuclear NMR spectroscopy. Furthermore, the retention of two and one weakly coordinated tht ligand on both complexes, particularly for **5**, confirms their inherent potential to serve as an alternative synthetic reagent for other Ir(III) phosphors. Figure 1 depicts

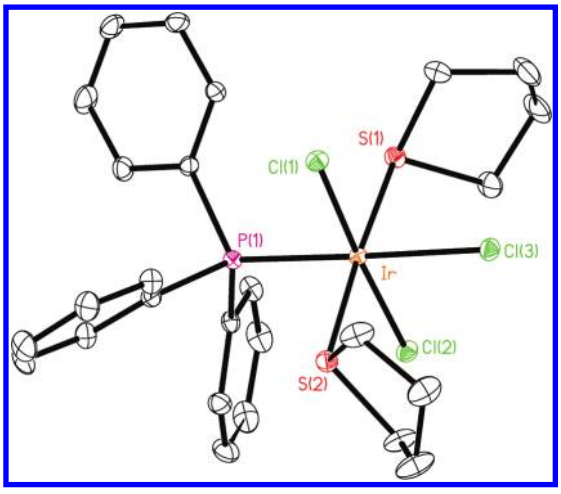


Figure 1. ORTEP diagram of **5** with ellipsoids shown at the 40% probability level. Selected bond distances (Å): Ir−P(1) = 2.2946(9), Ir−S(1) = 2.3562(9), Ir−S(2) = 2.3557(9), Ir−Cl(1) = 2.3779(9), Ir−Cl(2) = 2.3577(9), Ir−Cl(3) = 2.4174(8).

the ORTEP diagram of **5**. As can be seen, the three chloride ligands adopt a meridional arrangement around the Ir(III) atom. The PPh_3 is coordinated trans to the unique chloride, while the remaining axial sites are occupied by two tht ligands. For the bond distances, the Ir−Cl(3) length of 2.4174(8) Å is notably longer than those of the trans-substituted chlorides, i.e. Ir−Cl(1) = 2.3779(9) and Ir−Cl(2) = 2.3577(9) Å, confirming the greater trans influence of PPh_3 exerted on the central

dx.doi.org/10.1021/om300325y | Organometallics 2012, 31, 4349−4355

chloride, while both tht ligands on **5** adopt a puckered arrangement with an average Ir−S distance of 2.356 Å, which is similar to that of Ir(III) complexes bearing tht or other thioether ligands such as dithiane.[38,41]

Subsequently, a new Ir(III) complex of the formula $[Ir(dfppy)(tht)(PPh_3)Cl_2]$ (**7**) was then synthesized by heating the monosubstituted PPh_3 adduct **5** with 2-(2,4-difluorophenyl)pyridine (dfppyH) (cf. Scheme 2) or, alternatively, by heating a mixture of $IrCl_3(tht)_3$, dfppyH, and PPh_3 in a one-pot fashion in refluxing decalin. Figure 2 shows the

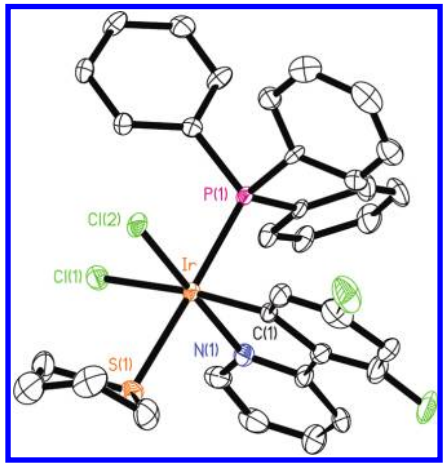


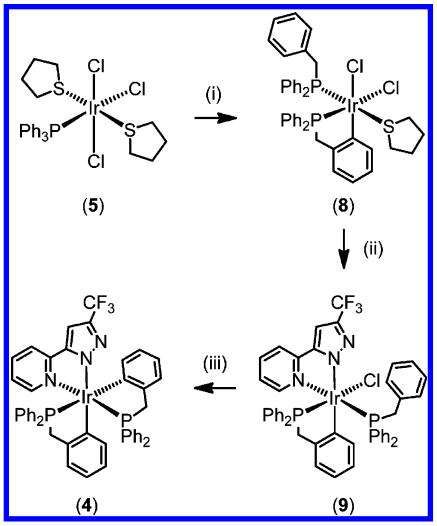
Figure 2. ORTEP diagram of **7** with ellipsoids shown at the 40% probability level. Selected bond distances (Å): Ir−P(1) = 2.306(3), Ir−S(1) = 2.407(3), Ir−N(1) = 2.091(10), Ir−C(1) = 1.972(12), Ir−Cl(1) = 2.489(3), Ir−Cl(2) = 2.377(3).

ORTEP diagram of **7**, for which the dfppy chelate and two chlorides assume a square disposition in a way similar to that for the analogous Ir(III) complex $[Ir(ppy)(Cl)_2(PPh_3)_2]$,[42] leaving the remaining axial sites occupied by one PPh_3 and one tht ligand. The Ir−Cl(1) distance of 2.489(3) Å is significantly longer than the Ir−Cl(2) distance of 2.377(3) Å, showing the difference induced by the greater trans influence imposed by the carbon donor versus the pyridyl donor.[43] Importantly, the trans PPh_3−Ir−tht ligand arrangement in **7** is notably different from the trans PPh_3−Ir−Cl arrangement observed in **5**, despite the possession of all three types of PPh_3, tht, and chloride ligands. Thus, this change in ligand arrangement was not controlled by the kinetics but by the more influential thermodynamic stability of the individual structure.

Finally, heating a mixture of **7** and fppzH in a 1:2 ratio gave the previously reported blue-emitting derivative **1** in 55% yield. An attempt to synthesize **7** directly from $IrCl_3(tht)_3$ without isolation, followed by addition of fppzH and heating in one pot, had given formation of identical product **1** in 32% yield. Remarkably, this recorded yield is much higher than the ∼20% yield of its original preparation that used no PPh_3 additive.[32] Thus, this single-pot strategy represents the optimized synthesis of the blue-emitting complex **1** and associated phosphors.[44]

Alternative Synthetic Pathway to 4. As reported in the previous section, the reaction of $[Ir(tht)_3Cl_3]$ with varying amounts of PPh_3 gave formation of the mono- and disubstitution products **5** and **6** (Scheme 2), while treatment of $[Ir(tht)_3Cl_3]$ with at least 2 equiv of bdpH in the presence of NaOAc led to the isolation of **3** (Scheme 1), for which the formation of cyclometalated bdp chelates was apparently caused by the added NaOAc promoter.[37] In an attempt to study the associated reaction sequences, i.e. phosphine addition versus cyclometalation, we then conducted the reaction of $[Ir(tht)_3Cl_3]$ with 3 equiv of bdpH in the absence of NaOAc with the hope of synthesizing the substitution products at different stages.[45] To our surprise, only the Ir(III) complex $[Ir(bdp)(bdpH)(tht)Cl_2]$ (**8**), which contains one coordinated bdpH, together with one cyclometalated bdp chelate, was isolated in lower yield (≤24%). Alternatively, upon switching from $[Ir(tht)_3Cl_3]$ to **5** as the Ir(III) source reagent, the respective reaction with bdpH afforded **8** in a much improved yield of 75%, while using the one-pot strategy, i.e. employing a mixed solution of $[Ir(tht)_3Cl_3]$, 1 equiv of PPh_3, and 2 equiv of bdpH, afforded the same product **8** in a comparable yield of 61%. These control reactions hinted that either the formation of **5** or the temporal coordination of PPh_3 is the key step leading to the efficient formation of diphosphine complex **8** (Scheme 3).

Scheme 3. Synthetic Route to the Ir(III) Metal Complex 4[a]



[a]Reagents and conditions: (i) 2 equiv of bdpH, decalin, 196 °C, 1 h; (ii) fppzH, Na_2CO_3, decalin, 160 °C, 0.5 h; (iii) AgOTf, $MeOCH_2CH_2OH$, 120 °C, 1 h.

The molecular geometry of **8** was unequivocally confirmed by single-crystal structure analyses. As shown in Figure 3, the two chlorides have a cis disposition, while the cyclometalated bdp chelate is located trans to these chlorides, and the remaining axial sites are occupied by the monodentate bdpH and one tht ligand. As usual, the Ir−C distance in the benzyl cyclometalate is short (ca. 2.064(3) Å), which points to enhanced covalent bonding character. The respective metallacycle is virtually coplanar, with the phenyl substituents on the phosphorus atom residing both above and below this plane. Variations of the Ir−Cl and Ir−P distances are somehow relevant to the trans effect discussed earlier. Remarkably, the Ir−P(1) distance of 2.2423(8) Å in **8** is notably shorter that the Ir−P(1) distance of 2.2946(9) Å in **5**. Both phosphorus atoms are trans with respect to the chloride, meaning that the shortening of this Ir−P distance in **8** is probably caused by the formation of a metallacycle, providing strong evidence with regard to its enhanced stability.

Application of **8** in synthesis was next probed with fppzH in the presence of Na_2CO_3. This reaction afforded the substitution product $[Ir(bdp)(bdpH)(fppz)Cl]$ (**9**), for which the tht and

dx.doi.org/10.1021/om300325y | Organometallics 2012, 31, 4349−4355

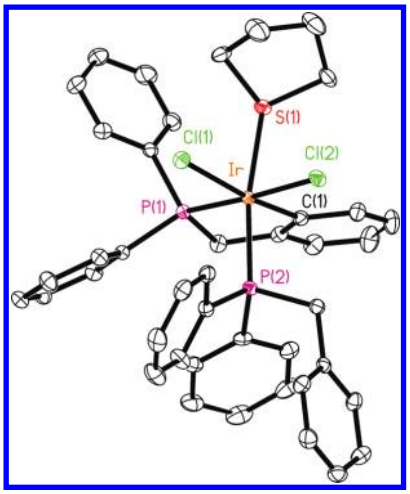


Figure 3. ORTEP diagram of **8** with ellipsoids shown at the 40% probability level. Selected bond distances: Ir−P(1) = 2.2423(8), Ir−P(2) = 2.3136(7), Ir−S(1) = 2.4411(8), Ir−Cl(1) = 2.4521(7), Ir−Cl(2) = 2.4358(7), Ir−C(1) = 2.064(3) Å.

one adjacent chloride were replaced by the incoming fppz chelate. The alternative, much simpler approach is to add 2 equiv of bdpH to $IrCl_3·3H_2O$ in 2-methoxyethanol, followed by addition of fppzH in the presence of Na_2CO_3, which afforded **9** in 40% yield, calculated using $IrCl_3·3H_2O$ as the limiting reagent. It appears that the chloride trans to the cyclometalated benzyl group in **8** was the preferable site for substitution. Since the aforementioned trans chloride is, in principle, more labile than the other chloride ligand, cf. Ir−Cl(1) = 2.4521(7) and Ir−Cl(2) = 2.4358(7) Å (Figure 3), we thus speculate that the transformation from **8** to **9** is under kinetic control.

Figure 4 depicts the ORTEP diagram of **9**, in which the remaining chloride still exhibits an identical bond distance, cf.

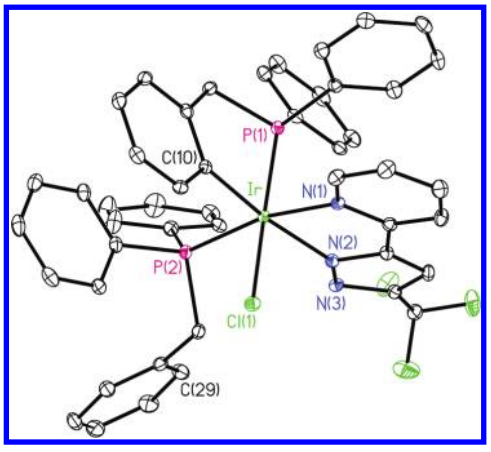


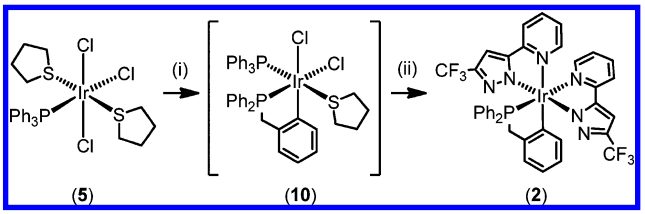
Figure 4. ORTEP diagram of **9** with ellipsoids shown at the 30% probability level. Selected bond distances: Ir−P(1) = 2.2598(8), Ir−P(2) = 2.3078(8), Ir−N(1) = 2.118(2), Ir−N(2) = 2.111(2), Ir−C(10) = 2.076(3), Ir−Cl(1) = 2.4312(7) Å.

Ir−Cl(1) = 2.4312(7) Å, implying the retention of the original bonding character and confirming the proposal of kinetic control. In fact, this last chloride could be removed with a scavenger, AgOTf, affording the expected cyclometalated product **4** in moderate yield (Scheme 3). Overall, this tranformation $[Ir(tht)_3Cl_3]$ → **5** → **8** → **9** → **4** is an alternative, but less desirable, synthetic protocol versus the original approach $[Ir(tht)_3Cl_3]$ → **3** → **4** shown in Scheme 1.[37] The disadvantage of the former lies in the extreme conditions required for the final cyclometalation of coordinated bdpH in **9** in comparison to the high-yield generation of **3**, with which the cyclometalation was easily executed in the presence of added NaOAc.

Improved Synthesis of 2. According to our previous report, blue-emitting phosphors such as **2** can be synthesized in 18−23% yield from the stepwise treatment of $IrCl_3(tht)_3$ with 1 equiv of bdpH, followed by heating in the presence of 2 equiv of fppzH and excess Na_2CO_3.[33] Unfortunately, this yield is much too low for scale-up industrial application and, thus, an alternative method is urgently needed, since its analogues are known to be superior for making true blue emitting OLEDs with decent efficiencies. Encouraged by the isolation of **8** and its capability of serving as a synthetic reagent, we initiated the preparation of $[Ir(bdp)(PPh_3)(tht)Cl_2]$ (**10**), in which the bdp chelate is expected to remain intact throughout the reaction, while the weakly coordinated PPh_3 would act as both stabilizer and leaving group at the same time.

One simple way to synthesize this intermediate **10** is via heating of **5** with an equal ratio or slight excess of bdpH in decalin (Scheme 4). However, after precipitating the mixture of

Scheme 4. Synthetic Route to the Ir(III) Complex 2[a]



[a]Reagents and conditions: (i) 1 equiv of bdpH, decalin, 196 °C, 1−2 h; (iii) 2 equiv of fppzH, Na_2CO_3, decalin, 196 °C, 12 h.

products by addition of hexane, we observed two sets of ^{31}P NMR signals at δ 3.62 and −14.93 with J_{PP} = 17.3 Hz and δ −3.44 and −16.05 with J_{PP} = 16.2 Hz, all with nearly equal intensities. In accordance with a previous report,[46] the signals at δ 3.62 and −14.93 can be identified as the coordinated bdpH and cyclometalated bdp chelate of **8**. This leaves the second set of signals at δ −3.44 and −16.05 to the coordinated PPh_3 and cyclometalated bdp chelate of **10**. Attempts to execute the reaction at lower temperature and shorter reaction time failed to cause any substantial change of this ^{31}P NMR signal ratio, which implied that the higher nucleophilicity of bdpH made the selective formation of **10** less desirable: i.e., showing rapid displacement of ligated PPh_3. Fortunately, upon switching the Ir(III) source to **6**, which possesses two coordinated PPh_3 groups, we were able to obtain a mixture that showed the **8**:**10** product ratio increased to 1:2.5, confirming both the spectral assignment and our speculation. Without further isolation, these mixtures of products were capable of reacting with added fppzH and Na_2CO_3 in decalin solution, giving the desired Ir(III) complex **2** in 35% yield. Furthermore, the one-pot procedure that employed $IrCl_3(tht)_3$ even increased the isolated yield to 44%, representing a significant improvement versus that reported in the literature.[33]

CONCLUSION

In summary, the present work reports a nonconventional method of synthesizing several Ir(III) phosphors that have been

dx.doi.org/10.1021/om300325y | Organometallics 2012, 31, 4349−4355

demonstrated great potential for fabrication of blue-emitting OLEDs.[32,33] The syntheses started with the conversion of $[IrCl_3(tht)_3]$ to **5** bearing one PPh_3 and two tht ligands. After that, treatment of **5** with dfppyH afforded **7** or, with a variable amount of bdpH gave either cyclometalated product **8** or **10**, depending on the reaction stoichiometry and conditions employed. Upon addition of fppzH chelate, these Ir(III) complexes **7**, **8**, and **10** were capable of yielding the desired blue phosphors **1**, **4**, and **2**, with which the fabrication of high-efficiency phosphorescent OLEDs is already well documented in the literature. For all intermediate species **5**, **7**, **8**, and **10**, the weakly coordinated PPh_3 and tht ligands are believed to be responsible for the successful preparation of these OLED phosphors in better yields.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving X-ray crystallographic data for the Ir(III) metal complexes **5**, **7**, **8**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ychi@mx.nthu.edu.tw (Y.C.); ytt@chem.sinica.edu.tw (Y.-T.T.); lsliao@suda.edu.cn (L.-S.L.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank both the National Science Council of Republic of China and the National Natural Science Foundation of China for financial support.

■ REFERENCES

(1) Chou, P.-T.; Chi, Y. *Chem. Eur. J.* **2007**, *13*, 380.
(2) Chi, Y.; Chou, P.-T. *Chem. Soc. Rev.* **2007**, *36*, 1421.
(3) Williams, J. A. G.; Wilkinson, A. J.; Whittle, V. L. *Dalton Trans.* **2008**, 2081.
(4) You, Y.; Park, S. Y. *Dalton Trans.* **2009**, 1267.
(5) Wong, W.-Y.; Ho, C.-L. *Coord. Chem. Rev.* **2009**, *253*, 1709.
(6) Zhou, G.-J.; Wang, Q.; Wong, W.-Y.; Ma, D.; Wang, L.; Lin, Z. *J. Mater. Chem.* **2009**, *19*, 1872.
(7) Chen, Z.-Q.; Bian, Z.-Q.; Huang, C.-H. *Adv. Mater.* **2010**, *22*, 1534.
(8) Zhou, G.; Wong, W.-Y.; Suo, S. *J. Photochem. Photobiol. C* **2010**, *11*, 133.
(9) Zhou, G.; Wong, W.-Y.; Yang, X. *Chem. Asian J.* **2011**, *6*, 1706.
(10) Lowry, M. S.; Bernhard, S. *Chem. Eur. J.* **2006**, *12*, 7970.
(11) Peng, Y.-K.; Lai, C.-W.; Liu, C.-L.; Chen, H.-C.; Hsiao, Y.-H.; Liu, W.-L.; Tang, K.-C.; Chi, Y.; Hsiao, J.-K.; Lim, K.-E.; Liao, H.-E.; Shyue, J.-J.; Chou, P.-T. *ACS Nano* **2011**, *5*, 4177.
(12) You, Y.; Lee, S.; Kim, T.; Ohkubo, K.; Chae, W.-S.; Fukuzumi, S.; Jhon, G.-J.; Nam, W.; Lippard, S. J. *J. Am. Chem. Soc.* **2011**, *133*, 18328.
(13) Zhang, K. Y.; Li, S. P.-Y.; Zhu, N.; Or, I. W.-S.; Cheung, M. S.-H.; Lam, Y.-W.; Lo, K. K.-W. *Inorg. Chem.* **2010**, *49*, 2350.
(14) Ho, M.-L.; Hwang, F.-M.; Chen, P.-N.; Hu, Y.-H.; Cheng, Y.-M.; Chen, K.-S.; Lee, G.-H.; Chi, Y.; Chou, P.-T. *Org. Biomol. Chem.* **2006**, *4*, 98.
(15) Zhao, Q.; Li, F.; Huang, C. *Chem. Soc. Rev.* **2010**, *39*, 3007.
(16) Kamtekar, K. T.; Monkman, A. P.; Bryce, M. R. *Adv. Mater.* **2010**, *22*, 572.
(17) Thompson, M. E. *MRS Bull.* **2007**, *32*, 694.
(18) Rausch, A. F.; Homeier, H. H. H.; Yersin, H. *Top. Organomet. Chem.* **2010**, *29*, 193.
(19) Chou, P.-T.; Chi, Y.; Chung, M.-W.; Lin, C.-C. *Coord. Chem. Rev.* **2011**, *255*, 2653.
(20) Yersin, H.; Rausch, A. F.; Czerwieniec, R.; Hofbeck, T.; Fischer, T. *Coord. Chem. Rev.* **2011**, *255*, 2622.
(21) Ulbricht, C.; Beyer, B.; Friebe, C.; Winter, A.; Schubert, U. S. *Adv. Mater.* **2009**, *21*, 4418.
(22) Chi, Y.; Chou, P.-T. *Chem. Soc. Rev.* **2010**, *39*, 638.
(23) Sasabe, H.; Kido, J. *Chem. Mater.* **2011**, *23*, 621.
(24) Nonoyama, M. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 767.
(25) Hwang, F.-M.; Chen, H.-Y.; Chen, P.-S.; Liu, C.-S.; Chi, Y.; Shu, C.-F.; Wu, F.-I.; Chou, P.-T.; Peng, S.-M.; Lee, G.-H. *Inorg. Chem.* **2005**, *44*, 1344.
(26) Zheng, Y.; Batsanov, A. S.; Edkins, R. M.; Beeby, A.; Bryce, M. R. *Inorg. Chem.* **2012**, *51*, 290.
(27) Tamayo, A. B.; Alleyne, B. D.; Djurovich, P. I.; Lamansky, S.; Tsyba, I.; Ho, N. N.; Bau, R.; Thompson, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 7377.
(28) St-Pierre, G.; Ladouceur, S.; Fortin, D.; Zysman-Colman, E. *Dalton Trans.* **2011**, *40*, 11726.
(29) Chien, C.-H.; Fujita, S.; Yamoto, S.; Hara, T.; Yamagata, T.; Watanabe, M.; Mashima, K. *Dalton Trans.* **2008**, 916.
(30) Tsurugi, H.; Fujita, S.; Choi, G.; Yamagata, T.; Ito, S.; Miyasaka, H.; Mashima, K. *Organometallics* **2010**, *29*, 4120.
(31) Baranoff, E.; Curchod, B. F. E.; Frey, J.; Scopelliti, R.; Kessler, F.; Tavernelli, I.; Rothlisberger, U.; Gratzel, M.; Nazeeruddin, M. K. *Inorg. Chem.* **2012**, *51*, 215.
(32) Yang, C.-H.; Cheng, Y.-M.; Chi, Y.; Hsu, C.-J.; Fang, F.-C.; Wong, K.-T.; Chou, P.-T.; Chang, C.-H.; Tsai, M.-H.; Wu, C.-C. *Angew. Chem., Int. Ed.* **2007**, *46*, 2418.
(33) Chiu, Y.-C.; Hung, J.-Y.; Chi, Y.; Chen, C.-C.; Chang, C.-H.; Wu, C.-C.; Cheng, Y.-M.; Yu, Y.-C.; Lee, G.-H.; Chou, P.-T. *Adv. Mater.* **2009**, *21*, 2221.
(34) Chiu, Y.-C.; Lin, C.-H.; Hung, J.-Y.; Chi, Y.; Cheng, Y.-M.; Wang, K.-W.; Chung, M.-W.; Lee, G.-H.; Chou, P.-T. *Inorg. Chem.* **2009**, *48*, 8164.
(35) Chatt, J.; Field, A. E.; Shaw, B. L. *J. Chem. Soc.* **1963**, 3371.
(36) Duff, J. M.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1972**, 2219.
(37) Hung, J.-Y.; Lin, C.-H.; Chi, Y.; Chung, M.-W.; Chen, Y.-J.; Lee, G.-H.; Chou, P.-T.; Chen, C.-C.; Wu, C.-C. *J. Mater. Chem.* **2010**, *20*, 7682.
(38) Lin, C.-H.; Chi, Y.; Chung, M.-W.; Chen, Y.-J.; Wang, K.-W.; Lee, G.-H.; Chou, P.-T.; Hung, W.-Y.; Chiu, H.-C. *Dalton Trans.* **2011**, *40*, 1132.
(39) Lin, C.-H.; Chang, Y.-Y.; Hung, J.-Y.; Lin, C.-Y.; Chi, Y.; Chung, M.-W.; Lin, C.-L.; Chou, P.-T.; Lee, G.-H.; Chang, C.-H.; Lin, W.-C. *Angew. Chem., Int. Ed.* **2011**, *50*, 3182.
(40) Chang, Y.-Y.; Hung, J.-Y.; Chi, Y.; Chyn, J.-P.; Chung, M.-W.; Lin, C.-L.; Chou, P.-T.; Lee, G.-H.; Chang, C.-H.; Lin, W.-C. *Inorg. Chem.* **2011**, *50*, 5075.
(41) Yamamoto, Y.; Sakamoto, S.; Ohki, Y.; Usuzawa, A.; Fujita, M.; Mochida, T. *Dalton Trans.* **2003**, 3534.
(42) Eum, M.-S.; Chin, C. S.; Kim, S. Y.; Kim, C.; Kang, S. K.; Hur, N. H.; Seo, J. H.; Kim, G. Y.; Kim, Y. K. *Inorg. Chem.* **2008**, *47*, 6289.
(43) Lyu, Y.-Y.; Byun, Y.; Kwon, O.; Han, E.; Jeon, W. S.; Das, R. R.; Char, K. *J. Phys. Chem. B* **2006**, *110*, 10303.
(44) Chang, C.-H.; Chen, C.-C.; Wu, C.-C.; Yang, C.-H.; Chi, Y. *Org. Electron.* **2009**, *10*, 1364.
(45) Lin, C.-H.; Lin, C.-Y.; Hung, J.-Y.; Chang, Y.-Y.; Chi, Y.; Chung, M.-W.; Chang, Y.-C.; Liu, C.; Pan, H.-A.; Lee, G.-H.; Chou, P.-T. *Inorg. Chem.* **2012**, *51*, 1785.
(46) Du, B.-S.; Lin, C.-H.; Chi, Y.; Hung, J.-Y.; Chung, M.-W.; Lin, T.-Y.; Lee, G.-H.; Wong, K.-T.; Chou, P.-T.; Hung, W.-Y.; Chiu, H.-C. *Inorg. Chem.* **2010**, *49*, 8713.