Synthesis of an iridium porphyrin amido complex

Jenkins Yin Ki Tsang and Kin Shing Chan

Abstract: A synthetic route for iridium porphyrin amido complexes has been established. Treatment of a THF solution of Ir(ttp)(CO)Cl (**1**) (ttp = 5,10,15,20-tetrakis(*p*-tolyl)porphyrinato dianion) with an aqueous mixture of NaOH and $NaBH_4$, followed by 2-iodoethanol leads to the clean formation of the β-hydroxyethyl complex Ir(ttp)(C_2H_4OH) (**2**) in 92% yield. Heating a pyridine solution of complex **2** in the presence of ca. 5–10 equiv. of phthalimide ($HNC_8H_4O_2$; HPhth) leads to the formation of Ir(ttp)(C_5H_5N)(CH_2CH_2Phth) (**3**). The replacement of pyridine by THF as the reaction solvent leads to the formation of the THF adduct Ir(ttp)(THF)(Phth) (**4**), which has been characterized spectroscopically. Heating a solution of **4** in pyridine leads to the formation of Ir(ttp)(C_5H_5N)(Phth) (**5**), which has been isolated in 72% yield. Complexes **3** and **5** have been characterized by X-ray crystallographic studies. Complexes **4** and **5** are rare examples of monomeric late transition metal-amido complexes and are the first examples of iridium-amido complexes featuring a porphyrin as a supporting ligand.

Key words: porphyrin, iridium amido, phthalimide.

Résumé : On a développé une méthode de synthèse pour les complexes iridium/porphyrine amido. Le traitement d'une solution de Ir(ttp)(CO)Cl (**1**) (ttp = dianion 5,10,15,20-tétrakis(*p*-tolyl)porphyrinato) dans du THF par un mélange aqueux de NaOH et de $NaBH_4$, suivi d'une réaction avec le 2-iodoéthanol conduit à une formation propre du complexe β-hydroxyéthyle Ir(ttp)(CH_2CH_2OH) (**2**) avec un rendement de 92 %. Le chauffage du composé **2**, en solution dans la pyridine, en présence d'environ 5 à 10 équivalents de phtalimide [[$C_6H_4(C{=}O)_2NH$], PhthH] conduit à la formation du Ir(ttp)(C_5H_5N) CH_2CH_2Phth (**3**). Le remplacement de la pyridine par du THF comme solvant conduit à la formation de l'adduit Ir(ttp) (THF)Phth (**4**) qui a été caractérisé par des méthodes spectroscopiques. Le chauffage d'une solution du composé **4** dans de la pyridine conduit à la formation du complexe Ir(ttp)(C_5H_5N)Phth (**4**) qui a été isolé avec un rendement de 72 %. Les complexes **3** et **5** ont été caractérisés par des études de diffraction des rayons-X. Les complexes **4** et **5** correspondent à de rares exemples de complexes monomères amido d'un métal de la fin de la période de transition et ce sont les premiers exemples de complexes iridium-amido comportant une porphyrine comme ligand support.

Mots-clés : porphyrine, iridium-amido, phtalimide.

[Traduit par la Rédaction]

Introduction

Transition metal-nitrogen covalently-bonded species are an interesting and important class of complexes.[1] They have been observed as key precursors and intermediates during important catalytic processes, such as amination of organic substrates,[2] hydroamination of olefins,[3] transfer hydrogenation,[4] amine dehydrogenation,[5] and ammoxidation.[6] In addition, metal-amidos can also effect nontrivial stoichiometric transformations such as C–H activation.[7] Late transition metal-amidos are by far less common than their early transition metal counterparts.[8] This is often rationalized by the hard-soft-acid-base theory, that hard amido or alkoxo ligands do not form strong bonds with late transition metals, which are generally considered soft. More specifically, there exists considerable electron repulsion between the filled $d\pi$ orbitals of the late transition metal and the $p\pi$ electrons of the amido ligand.[9] As a result, late transition metal-amidos are often reactive species that feature highly nucleophilic nitrogen atoms,[10] and the metal-nitrogen bonds often participate in amido exchange[11] or insertion chemistry.[10c,12] In addition, just like alkyl ligands, amido ligands are prone to undergo β-elimination.[13] Finally, amido ligands can also reductively eliminate in the presence of other suitable ligands.[14]

Our group has been researching carbon-hydrogen bond activation chemistry with iridium-porphyrin complexes to yield iridium porphyrin alkyls and acyls.[15] We have only once reported an Ir-phenoxide complex[16] but have never identified or isolated any Ir-N covalently-bonded species. This phenomenon is best explained by thermodynamics that late transition metal-carbon (alkyl or aryl) bonds are often stronger (by at least 20 kcal/mol) than the isoelectronic amido M–N bonds (1 cal = 4.184 J).[17]

Results and discussion

Our research group has attempted to construct iridium-nitrogen covalent bonds using the conventional metathesis reactions by treatment of the iridium-chloro species Ir(ttp) (CO)Cl[15] (**1**; ttp = 5,10,15,20-tetrakis(*p*-tolylporphyrinato

Received 14 April 2011. Accepted 27 June 2011. Published at www.nrcresearchpress.com/cjc on 22 November 2011.

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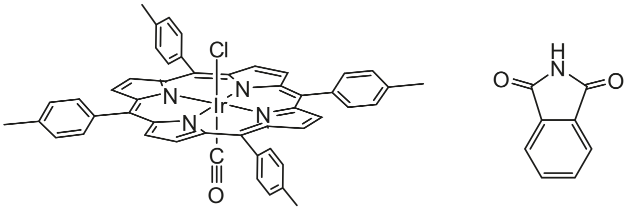
This article is part of a Special Issue to commemorate the International Year of Chemistry.

Fig. 1. Structure formula for Ir(ttp)(CO)Cl (**1**) and phthalimide (HPhth).



Ir(ttp)(CO)Cl **1**

Phthalimide (HPhth)

dianion; Fig. 1) with freshly-prepared lithium anilide, lithium diethylamide, or potassium phthalimide ($KC_8H_4NO_2$; KPhth). Disappointingly, these reactions only yielded mixtures of unidentifiable porphyrin-containing products without the incorporation of the amide onto the metal.

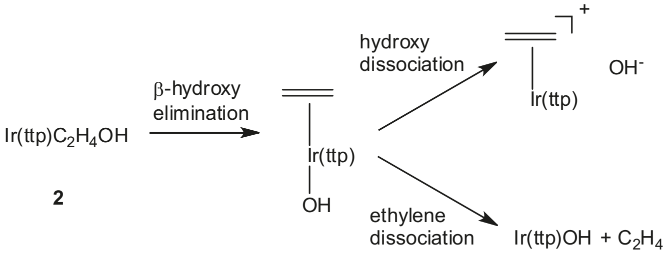
With complex **1** failing to serve as a viable source of a cationic iridium precursor for the synthesis of Ir-amidos, we decided to seek alternatives. Treatment of a THF solution of complex **1** with an aqueous solution of excess $NaBH_4$ in the presence of NaOH at 70 °C, followed by a slight excess of 2-iodoethanol, led to the formation of the β-hydroxyethyl complex Ir(ttp)(C_2H_4OH) (**2**) as a maroon solid in 92% yield (eq. [1]). The ^1H NMR spectrum of **2** closely resembles those of our recently reported rhodium complex Rh(ttp) (C_2H_4OH),[18] which has been demonstrated to be a precursor for the masked Rh(ttp)$^+$ cation after undergoing β-hydroxy elimination (Scheme 1).[18,19] Complex **2** is also closely related to a series of complexes with the general formula Rh(tpp) (CH_2CHROH) (tpp = 5,10,15,20-tetraphenylporphyrinato dianion), reported by Sanford et. al.,[20] as these complexes were synthesized via the reaction between the rhodium-porphyrin anion Rh(tpp)$^-$ and various epoxides.

[1] *IND, r, lf) = ″ : 1 :: .v11 − 126eq1.gif″*

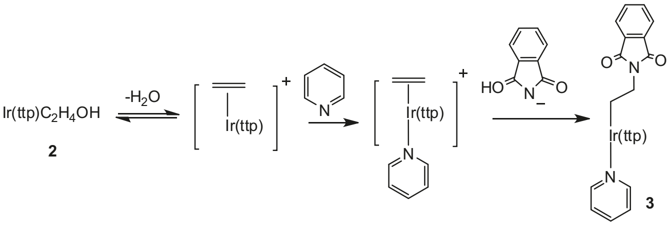
Phthalimide ($HNC_8H_4O_2$; HPhth; Fig. 1) is deemed a good initial candidate as an amido precursor, because (*i*) it is quite acidic, with the pK_a of the N–H of ca. 8, a desirable feature, as the successful incorporation of the amido ligand would require the loss of this proton and (*ii*) the nitrogen lone pair is delocalized in the bicyclic aromatic system, thereby greatly reducing possible dπ–pπ electron repulsion in the target Ir-phthalimido complex.

Heating a pyridine solution of **2** in an excess (10 equiv.) of phthalimide led to formation of a new porphyrin-containing species Ir(ttp)(C_5H_5N)(CH_2CH_2Phth) (**3**) in good yields (80%, eq. [2], as evidenced by a single new β-pyrrole proton signal at 8.50 ppm). Phthalimide has been deprotonated and symmetrically incorporated onto the final product, as indicated by a pair of 2-proton doublet of doublets at 7.07 and 7.16 ppm, respectively, attributable to the two different types of aryl protons. These signals have been shifted upfield from 7.77 and 7.87 ppm of free phthalimide. The presence of coordinated pyridine is indicated also by characteristic upfield-shifted signals. Intriguingly, in addition to these expected phthalimido and pyridine signals, two sets of 2-proton multiplets appear at –6.06 and –2.19 ppm, respectively. These signals suggest that the ethylene moiety is still present in this product. Purification of this new product was achieved by chromatography on Alumina, resulting in the isolation of a red-purple powder after solvent removal. Dark-red needle-shaped single crystals were obtained by slow diffusion of layered hexanes into a concentrated CH_2Cl_2 solution. An X-ray crystallographic analysis confirms the atom connectivity in **3**, as deduced from NMR spectroscopic data (Fig. 2). Table 1 lists the crystal data and collection parameters. Regrettably, the quality of the X-ray data precludes any meaningful discussion of metrical parameters of **3**. Nevertheless, the X-ray data indicate that the ethylene moiety has been retained. A possible explanation for the formation of **3** is the nucleophilic attack by phthalimido anion on the bound ethylene (Scheme 2).[12,18,19b,21] Consistent with previous related findings, compound **3** is thermally stable and does not undergo β-elimination,[22] with the crude reaction mixture remaining unchanged upon heating for a further 3 days at 150 °C.

Scheme 1. Possible reaction pathways initiated by **2**.



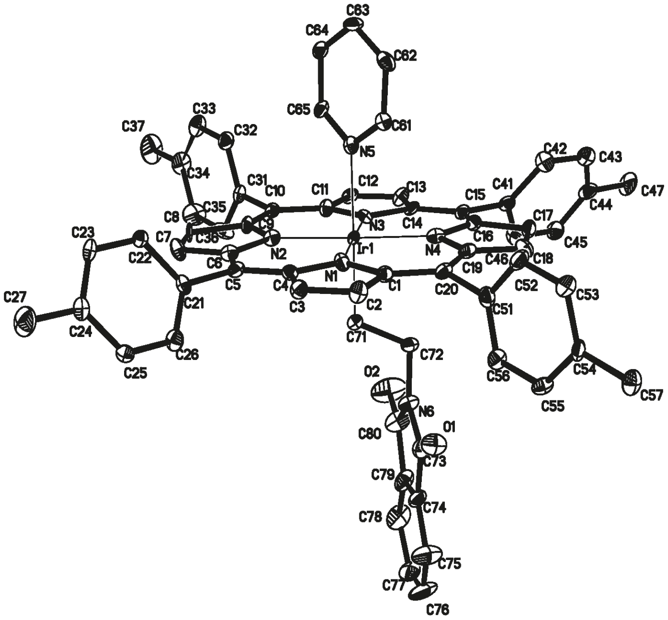
Scheme 2. Proposed mechanism for the formation of **3**.



[2] *IND, r, lf) = ″ : 1 :: .v11 − 126eq2.gif″*

We next employed THF, a polar aprotic but less coordinating solvent than pyridine. We reasoned that a weaker σ-donor opposite to the Ir-ethylene bond would weaken the synergic interaction between the metal and the π-acceptor,[23] thereby rendering the ethylene more prone to dissociation to allow preferred nucleophilic attack on the iridium centre rather than the carbon atom. Heating a THF solution of **2** in phthalimide at 150 °C cleanly yielded a single porphyrin-containing product. Pleasingly, the ^1H NMR spectrum of the crude product strongly suggests the exclusive formation of Ir(ttp) (THF)(Phth) (**4**) (eq. [3]). Specifically, phthalimide has been deprotonated and symmetrically incorporated, likely directly onto the metal center, as the aryl proton resonances now appear at 6.14 and 6.51 ppm, respectively, and are further upfield-shifted compared with the corresponding signals in complex **3**. The presence of coordinated THF is indicated by distinctive upfield signals at –2.33 and –0.70 ppm, respectively. Furthermore, no ethylene signals are present in the ^1H

Fig. 2. Solid-state molecular structure of 3 with 50% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity.



NMR spectrum of **3**. Unfortunately, the physical separation between **4** and the excess phthalimide proved to be problematic. Extraction with CH_2Cl_2–hexanes was unsatisfactory, washing with warm water led to the partial decomposition of **4** with the concomitant formation of new porphyrin-containing species, and chromatography on Alumina or silica yielded decomposition products.

[3] *IND, r, lf) = ″ : 1 :: .v11 − 126eq3.gif″*

Fortunately, under thermal conditions the THF ligand can be displaced by other ligands that yield more robust complexes. Thus, heating the crude mixture of **4** and phthalimide in neat pyridine at 100 °C for 15 h led to quantitative formation of Ir(ttp)(C_5H_5N)(Phth) (**5**), which was isolated in 78% yield as a red microcrystalline solid after chromatography on Alumina (eq. [4]). Single rod-shaped crystals were obtained from a CH_2Cl_2–hexanes bilayer, and an X-ray diffraction study confirmed the proposed structure for **5** (Fig. 3, Table 1). The distance between iridium and the phthalimido-N (Ir(1)–N(5)) is 2.083(2) Å, comparable to the iridium-pyridine distance (Ir(1)–N(6)) of 2.084(2) Å. The similarity between Ir–N covalent versus coordination bond distances has also been observed in a few other reported systems[11c,24] and could suggest low multiple-bond character between iridium and phthalimido. To our knowledge, complex **5** is the first example of an iridium porphyrin amido complex, whose structure has been studied by X-ray crystallography.

[4] *IND, r, lf) = ″ : 1 :: .v11 − 126eq4.gif″*

In conclusion, we have shown that the β-hydroxyethyl complex Ir(ttp)(C_2H_4OH) (**2**) can serve as a precursor towards novel iridium-nitrogen covalently bound species. We are currently exploring the scope of this reaction and examining the reactivity of **4** and **5**.

Experimental

General

Unless otherwise noted, all reagents were purchased from commercial suppliers and directly used without further purification. Hexanes were distilled from anhydrous $CaCl_2$. THF was distilled from sodium benzophenone ketyl. $CDCl_3$, used in the preparation of NMR samples, was distilled from CaH_2. Ir(ttp)Cl(CO) (**1**) was prepared according to the literature procedures.[15] Neutral Alumina (Merck, 70–230 mesh) / H_2O (10:1 *v*/*v*) was used for column chromatography.

NMR spectra were recorded at room temperature (RT) on Bruker DPX-300 or AV-400 spectrometers. ^1H NMR spectra are referenced to the residual protio isotopomer present in $CDCl_3$ (δ = 7.26 ppm) and ^{13}C NMR spectra are referenced to the natural-abundance carbon signal of the same solvent (δ = 77.23 ppm). Chemical shifts (δ) are reported as part per million (ppm) in (δ) scale downfield from TMS. Coupling constants (*J*) were reported in Hertz (Hz). High-resolution mass spectra (HRMS) were performed on a ThermoFinnigan MAT 95 XL mass spectrometer in fast atom bombardment (FAB) mode using 3-nitrobenzyl alcohol (NBA) matrix and CH_2Cl_2 as solvent or electrospray ionization (ESI) mode using MeOH:CH_2Cl_2 (1:1) as solvent.

Single X-ray crystal data were collected at 293 K using a Bruker AXS Kappa ApexII Duo diffractomter with Mo Kα radiation (λ = 0.71073 Å). Data collection and reduction were performed using ApexII software. Empirical multi-scan absorption correction was applied. Structures were solved by direct method and refined by full-matrix least-squares on F^2, using the SHELXTL program package. The presence of solvent accessible void was corrected by Platon/Squeeze program. Riding refinement was used for hydrogen treatment.

Preparation of Ir(ttp)C_2H_4OH (2)

A 250-mL sealable round-bottomed flask, equipped with a Rotaflo valve, was charged with Ir(ttp)(CO)Cl (46.2 mg, 50.0 mmol) and THF (50 mL). A 10 mL Schlenk tube was charged with aqueous NaOH (1 mol/L, 3 mL) and $NaBH_4$ (20.0 mg, 529 mmol). The two solutions were degassed separately for 15 min. The $NaBH_4$/NaOH solution was added to the solution of **1** using a cannula. The resulting mixture was sealed and heated to 70 °C for 2 h, after which a color change from red to dark orange-brown was observed. The reaction mixture was cooled to RT, and 2-iodoethanol (100 mg, 581 mmol) was added via a micropipette. The mixture was stirred for 15 h at RT, after which the color of the mixture did not change significantly. Solvents were removed in vacuo and the residue was washed with water, leaving behind Ir(ttp)(C_2H_4OH) (**2**) as a maroon solid. Compound **2** was further purified by chromatography on Alumina, eluting with CH_2Cl_2/hexanes (1:1). Yield 41.7 mg (92%). ^1H NMR (400 MHz, $CDCl_3$) δ: –5.32 (t, $^3J_{HH}$ = 7.2, 2H, Ir$CH_2$$CH_2$OH), –2.49 (t, $^3J_{HH}$ = 6.0, 1H, OH), –2.20 (m, 2H, Ir$CH_2$$CH_2$OH), 2.69 (s, 12H, CH_3), 7.53 (m, 8H, Ar H), 7.97 (d, $^3J_{HH}$ = 7.2, 4H, Ar H), 8.02 (d, $^3J_{HH}$ = 8.4, 4H, Ar H), 8.54 (s, 8H, β-pyrrole H).

Table 1. Crystal data and summary of data collection and refinement for **3** and **5**.

Param	**3**	**5**
Color, shape	Red needles	Red rods
Formula	$C_{63}H_{49}N_6O_2Ir$	$C_{61}H_{45}N_6O_2Ir$
Crystal size (mm)	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.20
Formula weight	1114.28	1086.23
Crystal system	triclinic	monoclinic
Space group	*P*-1	*P*2(1)/*c*
A (Å)	11.260 (2)	11.1705 (9)
B (Å)	13.461 (3)	17.3969 (14)
C (Å)	18.521 (4)	24.3961 (11)
A (°)	89.035 (4)	90
B (°)	73.592 (4)	100.4430 (10)
Υ (°)	81.450 (4)	90
V (Å^3)	2662.0 (10)	4662.4 (6)
Z	2	4
D_{calcd} (Mg/m^3)	1.390	1.547
Radiation (λ) (Å)	0.71073	0.71073
θ range (°)	1.53–25.00	1.85–25.00
F(000)	1124	2184
Reflections collected	29460	32806
Independent reflections	8540	8217
Data, restraints, parameters	8540, 0, 649	8217, 0, 631
Goodness of fit	1.186	1.088
Final $R_1{}^a$, $wR_2{}^b$ [$I > 2\sigma(I)$]	0.0735, 0.1778	0.0208, 0.0511
Final $R_1{}^a$, $wR_2{}^b$ (all data)	0.0829, 0.1809	0.0273, 0.0565
w_1, $w_2{}^c$	0.0000, 78.186	0.0259, 5.1729

$^aR_1 = \sum(||F_0| - |F_c||)/\sum|F_0|$.

$^bwR_2 = \{\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]\}^{1/2}$.

^{c}Weighting scheme $w^{-1} = \sigma^2(F_0^2) + (w_1P)^2 + w_2P$ where$P = (F_0^2 + 2F_c^2)/3$.

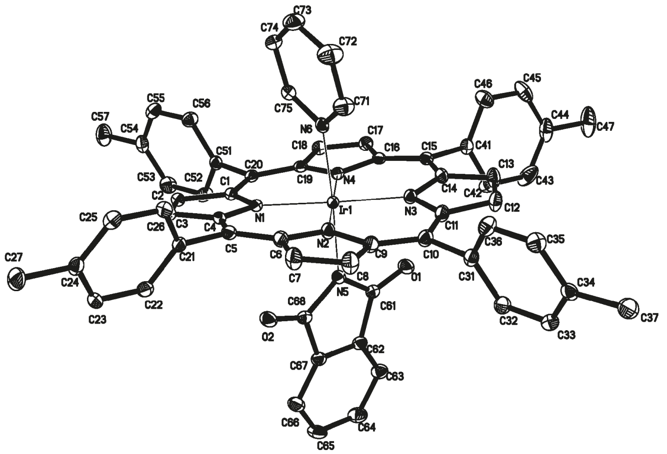


Fig. 3. Solid-state molecular structure of **5** with 50% thermal ellipsoids shown. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (º): Ir(1)–N(5) 2.083(2), Ir(1)–N(6) 2.084 (2), N(5)–C(61) 1.394(4), N(5)–C(68) 1.398(4), N(5)–Ir(1)–N(6) 176.51(9), C(61)–N(5)–C(68) 109.2(2), C(61)–N(5)–Ir(1) 125.75 (18), C(68)–N(5)–Ir(1) 124.69(18).

HRMS (FABMS) calcd. for [$C_{50}H_{41}N_4OIr$]$^+$: *m*/*z* 906.2904; found: *m*/*z* 906.2912.

Preparation of Ir(ttp)(C_5H_5N)($CH_2CH_2NC_4H_8O_2$) (3)

A glass tube equipped with a Rotaflo valve was charged with **2** (10.0 mg, 11.0 mmol), phthalimide (18.0 mg, 122 mmol), and pyridine (2 mL). The mixture was subjected to three freeze-pump-thaw cycles before being heated to 150 °C for 15 h, as the color changed from red-brown to red. Pyridine was removed in vacuo, and the mixture was analyzed by NMR spectroscopy. Hexanes were added to the $CDCl_3$ sample, and the solution was loaded onto an Alumina column, after which the column was eluted with CH_2Cl_2/hexanes (1:1). The major fraction was collected. Solvents were removed in vacuo, resulting in the deposition of **3** as a red microcrystalline powder. Yield 9.8 mg (80%). Single needle-shaped crystals suitable for X-ray crystallography were obtained from a CH_2Cl_2–hexanes bilayer. ^{1}H NMR (400 MHz, $CDCl_3$) δ: –6.06 (m, 2H, IrCH_2CH$_2$), –2.19 (m, 2H, IrCH$_2$CH_2), 2.18 (br d, 2H, py ortho H), 2.66 (s, 12H, CH$_3$), 5.31 (t, 7.53 (m, $^3J_{HH}$ = 7.2, 2H, py meta H), 6.17 (t, $^3J_{HH}$ = 7.6, 2H, py para H), 7.07 (dd, $^3J_{HH}$ = 5.4, $^4J_{HH}$ = 3.0, 2H, phthalimido Ar H), 7.16 (dd, $^3J_{HH}$ = 5.4, $^4J_{HH}$ = 3.0, 2H, phthalimido Ar H) 7.48 (m, 8H, Ar H), 7.97 (d, $^3J_{HH}$ = 7.2, 4H, Ar H), 8.05 (d, $^3J_{HH}$ = 7.6, 4H, Ar H), 8.50 (s, 8H, β-pyrrole H). ^{13}C NMR (100 MHz, $CDCl_3$) δ. HRMS (FABMS) calcd. for [$C_{63}H_{49}N_6O_2Ir$ – C_5H_5N]$^+$: *m*/*z* 1035.3119; found: *m*/*z* 1035.3130.

Preparation of Ir(ttp)(C_4H_8O)($NC_4H_8O_2$) (4)

A glass tube equipped with a Rotaflo valve was charged with **2** (10.0 mg, 11.0 mmol), phthalimide (18.0 mg, 122 mmol), and THF (2 mL). The mixture was subjected to three freeze-pump-thaw cycles before heated to 150 °C for

15 h, as the color changed from red-brown to red. THF was removed in vacuo, and the mixture was analyzed by NMR spectroscopy, which showed clean formation of **4**. Attempts to remove the excess phthalimide were not successful. ^{1}H NMR (400 MHz, $CDCl_3$) δ: –2.33 (m, 4H, THF), –0.71 (m, 4H, THF), 2.67 (s, 12H, CH_3), 6.14 (dd, $^3J_{HH} = 5.4$, $^4J_{HH} = 3.0$, 2H, phthalimido Ar H), 6.51 (dd, $^3J_{HH} = 5.4$, $^4J_{HH} = 3.0$, 2H, phthalimido Ar H), 7.49 (d, $^3J_{HH} = 8.0$, 8H, Ar H), 7.95 (d, $^3J_{HH} = 7.6$, 4H, Ar H), 8.11 (d, $^3J_{HH} = 8.0$, 4H, Ar H), 8.66 (s, 8H, β-pyrrole H).

Preparation of Ir(ttp)(C_5H_5N)($NC_4H_8O_2$) (5)

To a crude mixture of Ir(ttp)(C_4H_8O)($NC_4H_8O_2$) (**4**) and phthalimide was added pyridine (2 mL). The resulting solution was subjected to three freeze-pump-thaw cycles and then heated for 15 h at 100 °C, during which little color change was observed. The resulting mixture was dried in vacuo. Compound **5** was obtained in 78% yield as a red solid after chromatography on Alumina, eluting with CH_2Cl_2/hexanes (1:1). Single rod-shaped crystals suitable for X-ray crystallography were grown from a CH_2Cl_2–hexanes bilayer. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.13 (br d, 2H, py ortho H), 2.65 (s, 12H, CH_3), 5.05 (t, 7.53 (m, $^3J_{HH} = 7.2$, 2H, py meta H), 6.06 (t, $^3J_{HH} = 7.6$, 2H, py para H), 6.19 (dd, $^3J_{HH} = 5.4$, $^4J_{HH} = 3.0$, 2H, phthalimido Ar H), 6.54 (dd, $^3J_{HH} = 5.4$, $^4J_{HH} = 3.0$, 2H, phthalimido Ar H), 7.46 (m, 8H, Ar H), 7.86 (d, $^3J_{HH} = 7.2$, 4H, Ar H), 8.10 (d, $^3J_{HH} = 7.6$, 4H, Ar H), 8.64 (s, 8H, β-pyrrole H). HRMS (FABMS) calcd. for $[C_{61}H_{45}N_6O_2Ir]^+$: *m/z* 1086.3228; found: *m/z* 1086.3244.

Supplementary data

Text, tables, figures of crystallographic data for complexes **3** and **5** (CIF files), and ^{1}H and ^{13}C NMR spectra for complexes are available on the journal Web site (www.nrcresearchpress.com/doi/suppl/10.1139/v11-126). CCDC 831991 has also been deposited with the Cambridge Crystallographic Data Centre. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1Ez, UK; fax +44 1223 336033; or e-mail deposit@ccdc.cam.ac.uk).

Acknowledgements

We thank the Direct Grant of the Chinese University of Hong Kong for financial support. This paper is dedicated to Professor Tak-Hang Chan for his leadership always with words of encouragement.

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