

# Synthesis and characterization of phosphorescent cyclometalated Ir and Pt heteroleptic complexes using cyclophane-based chelates



B.K. Thilini Batagoda<sup>a</sup>, Peter I. Djurovich<sup>a</sup>, Stefan Bräse<sup>b</sup>, Mark E. Thompson<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, University of Southern California, Los Angeles, CA 90089, United States

<sup>b</sup> Institute of Organic Chemistry, Karlsruhe Institute of Technology, Kaiserstraße 12, 76131 Karlsruhe, Germany

## ARTICLE INFO

### Article history:

Received 14 March 2016

Accepted 26 April 2016

Available online 30 April 2016

### Keywords:

Phosphorescence  
Iridium  
Platinum  
Luminescent  
Cyclophane

## ABSTRACT

The synthesis and characterization of a series of neutral cyclometalated Pt(II) and Ir(III) heteroleptic complexes containing cyclophane substituted chelates is reported. The complexes have the general formula of (C<sup>^</sup>N)Pt(O<sup>^</sup>O) or (C<sup>^</sup>N)<sub>2</sub>Ir(O<sup>^</sup>O) where C<sup>^</sup>N is a monoanionic cyclophane ligand 2-([2.2]-paracyclophane-4-yl)pyridyl (pCpy) or 1-([2.2]-paracyclophane-4-yl)pyrazolyl (pCpz) and (O<sup>^</sup>O) is an ancillary ligand; acetylacetonato (acac) or dipivolylmethanato (dpm). The pCpyH and pCpzH ligand precursors were obtained as racemates due to the planar chirality of the cyclophane ring system. Two diastereomers of (pCpz)<sub>2</sub>Ir(acac), one with C<sub>1</sub> symmetry (Λ<sup>RS</sup>, Δ<sup>SR</sup>) and the other with C<sub>2</sub> symmetry (Λ<sup>RR</sup>, Δ<sup>SS</sup>) were isolated, whereas only one C<sub>1</sub> diastereomer was obtained for (pCpy)<sub>2</sub>Ir(acac). Inherent strain in the cyclophane core and transannular interaction between the bridged phenyl rings leads to a 250–400 mV cathodic shift in the oxidation potentials relative to analogous complexes with ppy or ppz ligands. The destabilization of the HOMO leads to a corresponding red shift in the absorption and emission spectra from the complexes with pCpy and pCpz ligands. The Pt and Ir complexes with pCpy ligands are strongly emissive at room temperature, whereas complexes with pCpz ligands are only weakly emissive as they still suffer from temperature-dependent nonradiative deactivation to metal-centered ligand field states.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

During last two decades, a significant research effort has focused on neutral Ir(III) and Pt(II) cyclometalated complexes due to their interesting photophysical and optoelectronic properties [1–3]. Heavy atom assisted spin–orbit coupling effect allows these molecules to perform efficient intersystem crossing (ISC) between singlet and triplet manifolds which ultimately lead to a high quantum yield of emission from the triplet state and shorter radiative lifetime compared to pure organics [4–6]. Thus, these materials could be used in wide variety of applications including emissive dopants in organic light emitting diodes (OLEDs) [7], sensitizers for electron transfer reactions [8], singlet oxygen sensitizers [9–12], photocatalysis [13–15] and as biological imaging reagents [16–20]. The lowest energy triplet state for these Ir(III) and Pt(II) cyclometalates consist of an admixture of ligand-centered triplet states (<sup>3</sup>LC) that is strongly perturbed by higher-lying metal-to-ligand charge-transfer (MLCT) states [2,3,21]. Therefore, the emission properties depend not only on the metal ion, but also on the cyclometalating chromophoric (C<sup>^</sup>N) ligand. Thus, it is desirable

to systematically understand how the modifications in the C<sup>^</sup>N ligand alter the properties of Ir and Pt cyclometalates.

Since the isolation of [2.2]-paracyclophane (pCp) by Brown and Farthing in 1949 [22], and its first synthesis by Cram and coworkers in 1951 [23], attention was drawn to its interesting chemical and physical properties [24]. Even though [2.2]-paracyclophane and its derivatives are widely used in catalysis [25,26] and polymer chemistry [27,28], applications related to optoelectronics are still not widely developed. The [2.2]-paracyclophane molecule consists of two eclipsed aryl rings that are held rigidly connected to each other at the para position by ethylene bridges. The aromatic rings are distorted into a shallow boat-like structures due to the strong steric repulsion with a separation that varies from a minimum of 2.78 Å at the bridgehead carbons to a maximum of 3.09 Å at the core [24]. Even though the aromatic systems are not conjugated to each other through bonds, they are coupled via a unique ‘transannular’ through space interaction between the two rings [29,30]. The distortion of the core due to high ring strain and transannular interaction between the π-systems makes this molecule an intriguing target for various chemical and photophysical studies.

The structure of [2.2]-paracyclophane provides a platform for the design and synthesis of substituted derivatives at various sites

\* Corresponding author.

E-mail address: [met@usc.edu](mailto:met@usc.edu) (M.E. Thompson).

on the molecular frame. Although substitution at the ethylene bridge is not very common, substitution at the aromatic ring leads to various species that show planar chirality [31,32]. Collectively, all these mentioned properties of [2.2]-paracyclophane enables access to a variety of synthons with broad tunability of their physical and chemical properties [33]. Indeed, the aforementioned properties make [2.2]-paracyclophane an interesting molecule to introduce into organometallic Pt and Ir systems so as to investigate the effect of cyclometalation on their structural and photophysical properties.

Herein, we have synthesized [2.2]-paracyclophane-substituted analogs of ppy and ppz ligands (pCpy-H and pCpz-H, respectively) and cyclometalated them to Pt and Ir. Structures of the resultant complexes are given in Fig. 1. The characterization of the heteroleptic complexes with acetylacetonate (acac) ancillary ligands is reported along with a detailed comparison of the photo-physical properties to their ppy and ppz congeners. The comparative analysis between the four complexes with their ppy and ppz analogs has allowed us to determine how the cyclophane ring system perturbs the overall properties of the cyclometalated complexes.

## 2. Experimental

### 2.1. Synthesis

Chemicals from commercial sources were used as received. All procedures were carried out in inert gas atmosphere despite the air stability of the complexes, the main concern being the oxidative and thermal stability of intermediates at the high temperatures of the reactions. Both pCpyH and pCpzH were synthesized according to previously reported procedures [34,35]. Metal complexes were synthesized initially by reacting respective metal chlorides with cyclometalating ligand (C^N) under Nonayama conditions [36,37], followed by treating the resultant intermediate with the ancillary ligand (L^X) acetylacetonate and a base in refluxing solvent.

#### 2.1.1. (pCpy)Pt(acac)

A 3-neck flask was charged with pCpyH (200 mg, 0.70 mmol), potassium tetrachloroplatinate(II) (116 mg, 0.28 mmol) and 15 mL of 3:1 mixture of 2-ethoxyethanol:water. All the reactants were degassed and heated to 70 °C for 16 h. The reaction was cooled to ambient temperature and the orange-yellow solid was precipitated into water and isolated by vacuum filtration. This solid was then placed in a new 3-neck flask charged with potassium carbonate (186 mg, 1.4 mmol) and charged with 15 mL of degassed 1,2-dichloroethane. The condenser was attached and the reaction was heated to 75 °C for 16 h after adding 2,4-pentanedione (150  $\mu$ L, 0.73 mmol). The reaction was then cooled to ambient temperature and the solvent was removed under vacuum. The resultant solid was subjected to column chromatography on silica gel 1:1 CH<sub>2</sub>Cl<sub>2</sub>:hexanes to give a bright yellow emissive solid (98 mg, 61%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ) 9.10 (d, *J* = 5.80 Hz,

1H), 7.78 (d, *J* = 4.05 Hz, 2H), 7.02 (d, *J* = 8.69 Hz, 2H), 6.58 (q, *J* = 8.83, 13.3 Hz, 2H), 6.28 (d, *J* = 7.66, 1H), 6.23 (d, *J* = 7.67, 1H), 6.01 (d, *J* = 7.73 Hz, 1H), 5.51 (s, 1H), 4.38 (ddd, *J* = 2.70, 10.01, 13.05 Hz, 1H), 3.87 (ddd, *J* = 2.47, 8.76, 14.08 Hz, 1H), 3.21–3.15 (m, 1H), 3.10 (ddd, *J* = 2.31, 9.72, 12.62 Hz, 1H), 3.05–2.96 (m, 2H), 2.91–2.85 (m, 1H), 2.81–2.75 (m, 1H), 2.00 (d, *J* = 11.32 Hz, 6H). *Anal.* for (pCpy)Pt(acac): found: C, 53.97; H, 4.37; N, 2.41%; calc.: C, 53.98; H, 4.36; N, 2.42.

#### 2.1.2. (pCpz)Pt(acac)

A 3-neck flask was charged with pCpzH (500 mg, 1.82 mmol), potassium tetrachloroplatinate(II) (300 mg, 0.78 mmol) and 75 mL of 3:1 mixture of 2-ethoxyethanol:water. The mixture was degassed and heated to 70 °C for 16 h. The reaction was cooled to ambient temperature and the pale yellow solid was precipitated into water and isolated by vacuum filtration. This solid was then placed in a new 3-neck flask charged with potassium carbonate (410 mg, 2.9 mmol) and charged with 45 mL of degassed 1,2-dichloroethane. The condenser was attached and the reaction was heated to 75 °C for 16 h after adding 2,4-pentanedione (0.12 mL, 1.16 mmol). The reaction was then cooled to ambient temperature and the solvent was removed under vacuum. The resultant solid was subjected to column chromatography on silica gel 1:1 CH<sub>2</sub>Cl<sub>2</sub>:hexanes to give a pale yellow solid (210 mg 47%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ) 8.13 (d, *J* = 2.63 Hz, 1H), 7.86 (d, *J* = 2.08 Hz, 1H), 7.13 (d, *J* = 6.61 Hz, 1H), 6.59–6.57 (m, 2H), 6.45 (d, *J* = 6.77 Hz, 1H), 6.27 (dd, *J* = 7.77, 19.0 Hz, 2H), 5.95 (d, *J* = 8.94 Hz, 1H), 5.51 (s, 1H), 4.39 (t, *J* = 10.6 Hz, 1H), 3.61 (q, *J* = 8.47, 14.5 Hz, 1H), 3.20–3.14 (m, 2H), 3.07 (t, *J* = 10.4 Hz, 1H), 2.94–2.88 (m, 1H), 2.84–2.71 (m, 2H), 1.98 (d, *J* = 1.32 Hz, 6H). *Anal.* for (pCpz)Pt(acac): found: C, 51.2; H, 4.29; N, 4.85%; calc.: C, 50.8; H, 4.26; N, 4.94.

#### 2.1.3. (ppz)Pt(dpm)

A 3-neck flask was charged with ppzH (0.18 mL, 1.3 mmol), potassium tetrachloroplatinate(II) (230 mg, 0.55 mmol) and 60 mL of 3:1 mixture of 2-ethoxyethanol:water. The mixture was degassed and heated to 70 °C for 16 h. The reaction was cooled to ambient temperature and the pale yellow solid was precipitated into water and isolated by vacuum filtration. This solid was then placed in a new 3-neck flask charged with potassium carbonate (180 mg, 1.3 mmol) and charged with 30 mL of degassed 1,2-dichloroethane. The condenser was attached and the mixture was heated to 75 °C for 16 h after adding 2,2,6,6-tetramethyl-3,5-heptanedione (0.21 mL, 1.00 mmol). The reaction was then cooled to ambient temperature and the solvent was removed under vacuum. The resultant solid was subjected to column chromatography on silica gel 1:1 CH<sub>2</sub>Cl<sub>2</sub>:hexanes gradient to give a pale yellow solid 145 mg (51%) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ ) 7.93 (d, *J* = 2.85 Hz, 1H), 7.75 (d, *J* = 2.25 Hz, 1H), 7.60 (dd, *J* = 2.92, 6.68 Hz, 1H), 7.12–7.08 (m, 3H), 6.52 (t, *J* = 4.29 Hz, 1H), 5.81 (s, 1H), 1.26 (d, *J* = 8.74 Hz, 9H). *Anal.* for (ppz)Pt(dpm): found: C, 46.05; H, 5.05; N, 5.35%; calc.: C, 46.06; H, 5.03; N, 5.37.

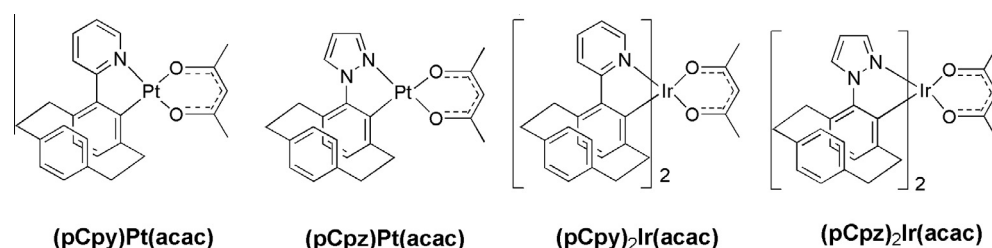


Fig. 1. Structures of (pCpy)Pt(acac), (pCpz)Pt(acac), (pCpy)<sub>2</sub>Ir(acac) and (pCpz)<sub>2</sub>Ir(acac).

Download English Version:

<https://daneshyari.com/en/article/1335024>

Download Persian Version:

<https://daneshyari.com/article/1335024>

[Daneshyari.com](https://daneshyari.com)