## Polyhedron 84 (2014) 136-143

Contents lists available at ScienceDirect

# Polyhedron

journal homepage: www.elsevier.com/locate/poly

# Synthesis and photophysical characterization of a bis-pincer osmium complex

Yifei Liu, Peter I. Djurovich, Ralf Haiges, Mark E. Thompson\*

Department of Chemistry, University of Southern California, Los Angeles, CA 90089, USA

#### ARTICLE INFO

Article history: Received 14 May 2014 Accepted 26 June 2014 Available online 11 July 2014

Keywords: Pincer ligand Osmium complex Dynamic NMR Phosphorescence Metal centered excited state

#### ABSTRACT

The neutral bis-pincer transition metal complex  $Os(PCP)_2$  (PCP = 2,6-(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Ph = C<sub>6</sub>H<sub>5</sub>) was prepared via two synthetic routes with up to 42% yield. The lemon-yellow complex is air stable as a neat solid and in solution, and is thermally stable as can be purified by high vacuum zone sublimation at 280-240-200 °C under 1  $\times$  10  $^{-6}$  torr. The pincer ligands coordinate in a pseudo-octahedral arrangement around the metal center. X-ray crystallography reveals that the complex is in pseudo-D<sub>2</sub> geometry symmetry due to the twist caused by the methylenes. NMR studies at varied temperatures between 223 and 343 K along with low temperature inversion recovery studies show the fluxional behavior and exchanging process between the two enantiomers ( $E_a = 8.6 \text{ kcal/mol}$ ). The Os(PCP)<sub>2</sub> shows no emission in solution at room temperature, but emits at 77 K in 2-MeTHF glass ( $\Phi = 60\%$ ). At room temperature, the neat solid of  $Os(PCP)_2$  shows yellow emission of 3% quantum yield. TDDFT predicted  $S_0 \rightarrow S_1$  transition shows that the lowest singlet state  $(S_1)$  is metal-ligand (the Os-Xylyl fragments) to ligand' (the PPh<sub>2</sub> fragments) charge transfer (ML-L'CT) in character with a small contribution from the higher lying metal centered (<sup>1</sup>MC) states. The large spin-orbit coupling constant of osmium leads to effective intersystem crossing to a triplet state with increased MC character. The DFT predicted triplet spin surface of Os(PCP)<sub>2</sub> indicates that the emission is dominated by <sup>3</sup>MC state. Significant Os-P bonds elongation at the lowest triplet excited state also strongly supports the conclusion.

© 2014 Elsevier Ltd. All rights reserved.

# 1. Introduction

Bis-terdentate chelated transition metal complexes such as  $[Ru(terpy)_2]^{2+}$ ,  $[Os(terpy)_2]^{2+}$ , and  $[Ir(terpy)_2]^{3+}$  with bis(2,2':6',2''terpyridine) (terpy) and related complexes have been intensively studied for their interesting photophysical, photochemical, and electrochemical properties, and potential applications in molecular electronics such as photoinduced electron and energy transfer organometallic rods, molecular wires and switches, and selfassembled light-harvesting systems [1–10]. The terdentate chelating ligands are structurally more appealing than bidentate chelating analogues for octahedral metal complexes as they lack optical isomers and enable a controllable linear arrangement for the design of functional molecular materials [11]. Terdentate carbene ligands have been employed in homo- and heteroleptic ruthenium complexes for interesting photophysical, especially photoluminescence properties [12–19]. Neutral or ionic heteroleptic iridium complexes containing two terdentate ligands of terpyridine,

N^C^N or C^N^C types of chelates have also attracted interest for their photophysical properties [20].

Among the array of choices for chelates of bis-terdentate transition metal complexes, a particular type of terdentate ligand, the pincer (pincer = L-X-L'-X-L, where X = CH<sub>2</sub>, NH, O, *etc.*) named after the chelating mode with the metal center is much less studied. Transition metal complexes chelated with pincer ligands were first reported in the 1970s and used diphosphine ligands of the general structure [2,6-(CH<sub>2</sub>PR<sub>2</sub>)2C<sub>6</sub>H<sub>4</sub>, PCP-H] (R = alkyl or aryl). These ligands can be readily cyclometalated onto metals such as Ni, Ir, Rh, Pt and Pd [21] and thus organometallic complexes containing mono-pincer chelates have been extensively studied thereafter, especially in catalysis chemistry [22,23]. To the best of our knowledge, the only example of a metal complex with bis-pincer coordination in literature is the main group metal complex  $Mg(P'CP')_2$ , where C is a metalated 2,6-xylyl group and P' is a PMe<sub>2</sub> substituent, reported by Muller and co-workers in 1994 [24].

Unlike in terpy-based ligands, where the pyridyl ligands (L) are conjugated through  $sp^2-sp^2$  linkages, conjugation between L-moieties in pincer ligands is interrupted by the  $sp^3$  hybridized linkages of the X-groups. Pincer ligands should therefore be poor acceptors since their unoccupied orbitals are at energies higher than that of







<sup>\*</sup> Corresponding author. Tel.: +1 2137404389. *E-mail address:* met@usc.edu (M.E. Thompson).

terpy. Similarly, the triplet energies of the pincer ligands should be higher than terpy based ligands due to the lack of conjugation in the molecular structure. Inspired by the literature studies on homoleptic and heteroleptic phosphorescent iridium complexes, the weak accepting properties and high triplet energy of the pincer ligands suggest that the phosphorescence of bis-pincer osmium complexes will show high energy emissions, significantly blueshifted from  $[Os(terpy)_2]^{2+} [25-27]$ . Therefore, we were interested in preparing the neutral bis-pincer based transition metal complex of  $Os(PCP)_2$ , with Os(II) metal center and typical PCP pincer ligand of  $[2,6-(CH_2PR_2)2C_6H_3]$  (R =  $C_6H_5$ ). Herein the synthetic routes, molecule structure, and photophysical characterization of the complex are fully examined.

# 2. Experimental

#### 2.1. Materials and methods

The syntheses were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled from sodium benzophenone (hexanes, THF), or calcium hydride (2-propanol). The starting materials  $OsCl_2(PPh_3)_3$  and  $1,3-(PPh_2 CH_2)_2C_6H_4$  (PCP-H) were prepared according to literature methods [28–30]. Other chemicals and solvents were ordered from Sigma-Aldrich<sup>®</sup>, and used as received. <sup>1</sup>H NMR, <sup>31</sup>P NMR, gCOSY NMR at 223 K, inversion recovery NMRs at 233 K, and VT-<sup>1</sup>H NMR spectra were measured by Varian 600 NMR Spectrometer. The <sup>13</sup>C NMR cannot be resolved due to the poor solubility of  $Os(PCP)_2$ . The chemical shifts were referenced to a deuterated solvent. Mass spectra were obtained on a Shimadzu LCMS-2020 quadrupole mass spectrometer equipped with a column oven ( $T = 40 \,^\circ$ C), a PDA photodetector (200–800 nm) and a MS spectrometer (LC–MS 2020; *m/z* range: 0–2000; ionization modes: ESI/APCI).

# 2.2. Synthesis of $Os(PCP)_2$ (PCP = 2,6-(PPh\_2CH\_2)\_2C\_6H\_3)

Route 1: The Schlenk tube with  $OsCl_2(PPh_3)_3$  (240 mg. 0.23 mmol) and PCP-H (327 mg, 0.69 mmol) was evacuated for 30 min. Then 80 ml of dry and deaerated 2-propanol was added. The solution mixture was refluxed for 24 h, cooled to room temperature, and filtered over Al<sub>2</sub>O<sub>3</sub> plug. The filtrate solution was then evaporated over rotavap. The solid residue was washed with hexanes and diethyl ether. Then the dried solid was dissolved in 15 ml THF, and precipitated with dropwise addition of 30 ml hexanes. The precipitate was dried under vacuum and obtained as 110 mg lemon yellow solid (42%). Route 2: OsCl(PPh<sub>3</sub>)(PCP) was synthesized following literature process and isolated in 50% yield. The AgOTf (27 mg, 0.10 mmol) and OsCl(PPh<sub>3</sub>)(PCP) (100 mg, 0.10 mmol) were reacted in THF at room temperature for 1 h. The solution was filtered, and the solvent was evaporated. The in situ generated Os(OTf)(PPh<sub>3</sub>)(PCP) (90% yield) was directly used for the next step without further purification. The Schlenk tube with Os(OTf)(PPh<sub>3</sub>)(PCP) (100 mg, 0.09 mmol) and PCP-H (43 mg, 0.09 mmol) was evacuated for 30 min. Then 20 ml of dry and deaerated 2-propanol was added. The solution mixture was refluxed for 24 h, cooled to room temperature, and then followed by the same workup as in Route 1 (yield based on  $OsCl_2(PPh_3)_3 = 31\%$ ).

<sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>, 343 K):  $\delta$  = 7.39 (d, *J* = 7.2 Hz, 4H, xylyl CH),  $\delta$  = 7.31 (t, *J* = 6.6 Hz, 2H, xylyl CH),  $\delta$  = 6.92–6.73 (m, 40H, PPh<sub>2</sub>),  $\delta$  = 3.60 (s, 8H, CH<sub>2</sub>). <sup>1</sup>H NMR (600 MHz, C<sub>7</sub>D<sub>8</sub>, 223 K):  $\delta$  = 7.83 (m, 4H, o-Ph),  $\delta$  = 7.63 (d, *J* = 3.6 Hz, 4H, o-Ph),  $\delta$  = 7.54 (d, *J* = 7.2 Hz, 4H, xylyl CH),  $\delta$  = 7.48 (t, *J* = 7.2 Hz, 2H, xylyl CH),  $\delta$  = 7.34 (t, 4H, *J* = 6.6 Hz, m-Ph),  $\delta$  = 6.82 (t, 4H, *J* = 7.2 Hz, m-Ph),  $\delta$  = 6.68 (d, *J* = 6.0 Hz, 4H, o-Ph),  $\delta$  = 6.41 (t, *J* = 6.6 Hz, 4H, p-Ph),  $\delta$  = 5.76 (t, *J* = 7.2 Hz, 4H, m-Ph),  $\delta$  = 5.49 (d, *J* = 6.0 Hz, 4H, o-Ph),

δ = 3.62, 3.52 (AB,  $J_{AB} = 14.4$  Hz, 8H, CH<sub>2</sub>). <sup>31</sup>P NMR (243 MHz, C<sub>6</sub>D<sub>6</sub>, 343 K): δ = 6.1 (s). <sup>31</sup>P NMR (243 MHz, C<sub>7</sub>D<sub>8</sub>, 223 K): δ = 11.2 (s). LC–MS ESI (*m*/*z*): 1138.50 ([M], calc. 1138.28).

#### 2.3. X-ray crystallography

The X-ray intensity data were measured on a Bruker APEXDUO CCD system using radiation from a Mo Ka fine-focus tube  $(\lambda = 0.71073 \text{ Å})$  with a TRIUMPH monochromator. A clear yellow pear shape specimen of  $C_{64}H_{54}OsP_4$ , approximate dimensions 0.16 mm  $\times$  0.09 mm  $\times$  0.04 mm, was used for the X-ray crystallographic analysis. A total of 2520 frames were collected. The frames were integrated using the Bruker SAINT V8.18C software. The integration of the data using a triclinic unit cell yielded a total of 75643 reflections to a maximum  $\theta$  angle of 27.51 (0.68 Å resolution), of which 11025 were independent (average redundancy 7.761, completeness = 95.5%,  $R_{int}$  = 7.75%). The final cell constants of *b* = 14.1378(12) Å, a = 12.6896(11) Å, c = 14.7794(13) Å, volume = 2511.0(4) Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of 9013 reflections above  $2\theta \sigma(I)$  with  $1.40 < 2\theta < 27.51^{\circ}$ . Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.766.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group triclinic  $P\bar{1}$ , with Z = 2 for the formula unit,  $C_{64}H_{54}OsP_4$ . The final anisotropic full-matrix least-squares refinement on  $F^2$  with 415 variables converged at  $R_1 = 6.78\%$ , for the observed data and  $wR_2 = 11.25\%$  greater than  $2\sigma(F^2)$ . The goodness-of-fit was 1.072. The largest peak in the final difference electron density synthesis was  $1.352 \text{ e}^-/\text{Å}^3$  and the largest hole was  $-1.041 \text{ e}^-/\text{Å}^3$ . On the basis of the final model, the calculated density was  $1.504 \text{ g/cm}^3$  and F(000),  $1148 \text{ e}^-$ .

# 2.4. Photophysical characterization

The UV–Vis spectra were recorded on a Hewlett–Packard 4853 diode array spectrometer. Steady-state emission measurements were performed using a QuantaMaster model C-60SE spectrofluorimeter (Photon Technology International) with an excitation wavelength of 350 nm in 2-MeTHF glass (77 K), in the solid state, and in the PMMA film under N<sub>2</sub> protection. Phosphorescent lifetimes were measured by time-correlated single-photon counting with IBH Fluorocube instrument equipped with a 405 nm LED excitation source. Quantum yield (298 K) was measured using a Hamamatsu C9920 system equipped with a xenon lamp, calibrated integrating sphere, and Model C10027 photonic multichannel analyzer. The low temperature (77 K) quantum yield was determined relative to the quantum yield of  $Ir(ppy)_3$  at 77 K ( $\emptyset$  = 1) [27].

#### 2.5. Theoretical calculations

The theoretical calculations were carried out by Schrödinger 2013 Materials Science Suite, using the density function theory (DFT) with Lee-Yang-Parr correlation functional B3LYP. The basis set used was LACVP\*\*. Time-dependent DFT (TD-DFT) calculations were performed with GAUSSIAN 03 program to understand more about the ground state to excited states transitions of the complex. The same hybrid functional of B3LYP was employed, and the basis set was LANL2DZ/6-31G\*.

#### 2.6. Electrochemistry

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed using an EG&G Potentiostat/Galvanostat model 283. Dry DMF was used as solvent under a  $N_2$  atmosphere with 0.1 M tetra(*n*-butyl)ammonium

hexafluorophosphate as the supporting electrolyte. A glassy carbon working electrode and a platinum counter electrode were used, with a silver wire as the pseudoreference electrodes. The oxidation potential was measured relative to a ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) redox couple as an internal standard. Electrochemical reversibility is determined by cyclic voltammetry.

# 3. Results and discussion

# 3.1. Synthetic routes of Os(PCP)<sub>2</sub>

The bis-pincer complex  $Os(PCP)_2$  was prepared in a reaction of excess PCP-H ligand precursor (3 eq) with  $OsCl_2(PPh_3)_3$  (1 eq) in refluxing anhydrous 2-propanol for 24 h (Scheme 1, Route 1). During the course of the reaction the solution changed color from green to purple. After filtration and workup, the complex was isolated as a lemon-yellow powder (42% yield) that is air-stable as a neat solid and in solution. However, the solubility of  $Os(PCP)_2$  in general is poor, being most soluble in aromatic solvents. The complex is thermally stable as crystals can be obtained by gradient sublimation at 280-240-200 °C under vacuum (1 × 10<sup>-6</sup> torr).

The stepwise preparation of  $Os(PCP)_2$  was also investigated. A reaction between PCP-H (1 eq) and  $OsCl(PPh_3)(PCP)$  (1 eq) [31] in 2-propanol, surprisingly, only results in the formation of an intractable black solution. However, on the basis of previous work with related Ru complexes [32], substitution of chloride with triflate to form  $Os(OTf)(PPh_3)(PCP)$ , followed by reaction with PCP-H (Route 2) led to  $Os(PCP)_2$  in overall 31% yield (based on  $OsCl_2$  (PPh\_3)<sub>3</sub>). Interestingly, in the case of the Ru cogener of  $Os(PCP)_2$  one ligand forgoes metalation and instead forms an agostic C-H···Ru interaction, even despite several attempts at deprotonation with strong bases [32,33]. Apparently, for osmium the metal-C bond is strong enough that deprotonation of the aryl can occur without added base to form a stable dimetalated product.

# 3.2. X-ray crystallography

X-ray diffraction analysis was carried out on a crystal of  $Os(PCP)_2$  obtained from sublimation. The unit cell of  $Os(PCP)_2$  crystal contains a pair of enantiomers in a triclinic  $P\bar{1}$  space group. Perspective drawings of the complex are depicted in Fig. 1 (left, middle). Selected bond distances and angles are given in Table 1. The molecular geometry of  $Os(PCP)_2$  shows that the pincer ligands are arranged in pseudo-octahedral environment around the metal center (Fig. 1, left). The Os(1)-C(31) and Os(1)-C(47) bond distances (2.151(7) Å and 2.149(7) Å respectively) are longer than the Os—C bond distances observed for monopincer osmium complex  $OsCl(PPh_3)(PCP)$  (2.04(1) Å) [31]. The Os—C bonds are elongated due to the trans-effect between the two opposing aryl rings, a

feature absent in OsCl(PPh<sub>3</sub>)(PCP). The bond lengths of the four Os—P bonds are nearly identical, ranging between 2.3348(19) Å and 2.3419(19) Å, and only slightly longer than the Os—P bond lengths of the OsCl(PPh<sub>3</sub>)(PCP) (2.313(4) Å and 2.312(4) Å). Likewise, comparison with [OsCl(=C=CHPh)(PPh<sub>3</sub>)(PCP)], where the vinylidene substituent (trans to Cl) is strongly electron-withdrawing, shows similar distances for the Os–C<sub>PCP</sub> (2.133(5) Å) and Os–P<sub>PCP</sub> (2.3889(14) Å and 2.3547(15) Å) bonds [31]. The phenyl rings in Os(PCP)<sub>2</sub> are arranged around the complex into two distinct sets of pairs, designated A and B (Fig. 1, middle). The phenyl rings in the A-type pairs are slip-stacked and in close enough proximity to undergo  $\pi$ – $\pi$  interactions (shortest C—C distance = 3.2 Å) whereas rings in the B-type pairs are further apart (shortest C—C distance 3.7 Å) and have no  $\pi$ -overlap.

The deviation from an ideal octahedral geometry in  $Os(PCP)_2$  is due to small chelate bite angles in the PCP ligand (average C-Os- $P = 76.5^{\circ}$ ). Thus, while the axially ligated carbon atoms are near linear  $[C(31)-Os(1)-C(47) = 178.60(3)^{\circ}]$ , bond angles for the trans disposed P(1)-Os(1)-P(3) and P(2)-Os(1)-P(4) are 152.21(7)° and 153.75(7)°, respectively. The pseudo tetrahedral configuration of the bridging methylenes (average  $P-CH_2-C$  angle = 105°) causes the phosphines in the PCP ligand to twist in a transoid conformation away from the plane of the xylyl group (average  $C_{OS}$ -C-CH<sub>2</sub>-P dihedral angle = 24.6°). A projection view down the C(31)-Os(1)–C(47) axis (Fig. 1, right) illustrates the relative orientation of the xylyl moieties with respect to the phosphines. The xylyl planes are tilted 46° with respect to each other, while the projected angle of the two P-Os-P planes of the PCP ligands is perpendicular. The transoid twist in the PCP ligands leads to a pseudo- $D_2$  symmetry for the complex, and hence the presence of  $\Delta$  and  $\Lambda$ enantiomers, as opposed to the  $D_{2d}$  symmetry found in  $M(terpy)_2^{n+1}$ complexes [1].

#### 3.3. NMR characterization

The Os(PCP)<sub>2</sub> complex undergoes a dynamic exchange process in fluid solution at ambient temperatures. The <sup>1</sup>H NMR spectrum measured in C<sub>6</sub>D<sub>6</sub> at 298 K shows broad and featureless resonances for the phenyl rings ( $\delta$  = 6.10–7.10 ppm) and only one singlet ( $\delta$  = 3.64 ppm) for the eight diastereotopic methylene protons (Fig. SI-1). No signal is observed in <sup>31</sup>P NMR at 298 K. NMR spectra recorded in C<sub>6</sub>D<sub>6</sub> at higher temperatures are more structured. For example, the <sup>31</sup>P NMR at 343 K shows a single resonance ( $\delta$  = 6.1 ppm) indicating that the phosphorus atoms on the pincer ligands are in equivalent environments (Fig. SI-2). Sharp resonances are also observed for the xylyl protons ( $\delta$  = 7.39, d, *J* = 7.2 Hz, 4H;  $\delta$  = 7.31, t, *J* = 6.6 Hz, 2H) while three broad signals further upfield ( $\delta$  = 6.73-6.92 ppm) are assigned to protons on freely rotating phenyl rings of the PCP ligand (Fig. SI-3).



Scheme 1. The synthetic route for Os(PCP)<sub>2</sub>.



**Fig. 1.** Two perspective views of Os(PCP)<sub>2</sub> shown in 50% probability thermal ellipsoids (left, middle). Hydrogen atoms and the phenyl rings on phosphorus (left) are omitted for clarity. Projection view down the C(31)–Os(1)–C(C47) axis of Os(PCP)<sub>2</sub> (right). Solid and dashed lines represent the xylyl planes.

 Table 1

 Selected bond lengths (Å) and angles (degree) of Os(PCP)<sub>2</sub>.

Bond lengths (Å)			
Os(1)-C(31) Os(1)-P(1) Os(1)-P(3)	2.151(7) 2.338(2) 2.341(2)	Os(1)-C(47) Os(1)-P(2) Os(1)-P(4)	2.149(7) 2.3348(19) 2.3419(19)
Bond angles (°)			
P(1)-Os(1)-P(3) P(1)-Os(1)-C(47) P(3)-Os(1)-C(47) C(31)-Os(1)-C(47)	152.21(7) 76.1(2) 76.1(2) 178.60(3)	P(2)-Os(1)-P(4) P(2)-Os(1)-C(31) P(4)-Os(1)-C(31)	153.75(7) 77.1(2) 76.7(2)

Highly resolved NMR spectra are observed at low temperature (223 K) in toluene-d<sub>8</sub> ( $C_7D_8$ ) (Figs. SI-4-6). The <sup>31</sup>P NMR shows a single resonance ( $\delta$  = 11.2 ppm) while splitting of the diastereotopic methylenes is clearly evident in the <sup>1</sup>H NMR ( $\delta$  = 3.62, 3.52 ppm,  $J_{AB}$  = 14.4 Hz). Eight well-resolved resonances, along with two more signals obscured by residual protons on the solvent, are observed for the protons on the PPh<sub>2</sub> mojeties indicating that the phenyl rings are situated in two distinct environments. Correlations between the various protons of the phenyl rings are clearly revealed in the gCOSY spectrum. Resonances appear upfield for ortho (o)-, meta (m)- and para (p)-protons on one set of phenyls at  $\delta_0$  = 5.49 ppm,  $\delta_m$  = 5.76 ppm,  $\delta_p$  = 6.41 ppm and  $\delta_{m'}$  = 6.82 ppm with the remaining signal at  $\delta_{o'}$  = 7.63 ppm. Signals from the other set of phenyls appear downfield ( $\delta_0$  = 6.68 ppm,  $\delta_m$  = 6.95 ppm,  $\delta_p$  = 7.05 ppm,  $\delta_{m'}$  = 7.34 ppm and  $\delta_{o'}$  = 7.83 ppm). The NMR data is consistent with the complex being in a D<sub>2</sub> configuration similar to what is found in the crystal structure. The upfield resonances are tentatively assigned to protons shielded by the  $\pi$ -stacked phenyl rings labelled A in Fig. 1 (middle) whereas the other signals belong to the B-type phenyls. The exchange process at 233 K was probed further by performing an inverse recovery experiment (Figs. SI-7 and 8).[34] A 180° pulse applied to the ortho-proton resonance at  $\delta$  = 5.49 ppm was found to transfer magnetization to all the other ortho-protons in the phenyl rings during relaxation. This behavior indicates that the exchange involves simultaneous rotation of the phenyl rings and interchange between the A- and B-sites (racemization).

Variable temperature <sup>1</sup>H NMR measurements in  $C_7D_8$  were carried out between 223 K and 343 K (Figs. SI-9 and 10). The xylyl protons display sharp signals throughout the entire temperature range, undergoing only slight changes in bandwidth and a gradual shift upfield with increasing temperature. In contrast, resonances from the phenyl protons collapse into the baseline as temperature is increased from 223 to 283 K. Upon further warming to 343 K these aromatic signals reappear as a broad set of multiplets between  $\delta = 6.4$  and 6.8 ppm. In addition, the doublet pattern



Fig. 2. Variable temperature  $^1\text{H}$  NMR spectra (600 MHz,  $C_7D_8)$  for the methylene protons of Os(PCP)\_2.

expected for a diastereotopic methylene protons converts to single coalesced resonance on warming from 223 to 273 K (Fig. 2). This signal sharpens as temperature increases from 273 to 343 K.

A model for the fluxional behavior leading to racemization of Os(PCP)<sub>2</sub> is illustrated in Fig. 3. At 223 K, Os(PCP)<sub>2</sub> can be represented as  $\Delta$ - or  $\Lambda$ -enantiomers with D<sub>2</sub> symmetry undergoing slow exchange of the A- and B-type phenyls on the NMR timescale (see SI). As temperature increases, the rate of exchange increases until coalescence is achieved at 273 K for the methylenes and 283 K for the phenyls (Fig. SI-9). Above this temperature, the diastereotopic methylene protons undergo a fast exchange process as the phenyl rings rotate more rapidly. At 343 K, the enantiomers are in rapid exchange and display an NMR spectrum consistent with a complex in a pseudo-D<sub>2d</sub> symmetric environment. Rate constants (k) were calculated by analyzing the NMR spectra for the methylenes at temperatures between 248 and 268 K. An Arrhenius plot of  $\ln(k)$  versus 1/T gives a good linear fit, with  $r^2 = 0.966$ (Fig. SI-11) [35]. The line-shape analysis indicates that the activation energy for racemization of Os(PCP)<sub>2</sub> is 8.6 kcal/mol.

## 3.4. Electrochemistry

The electrochemical properties of  $Os(PCP)_2$  were examined by cyclic voltammetry and differential pulse voltammetry in  $CH_2Cl_2$  solution (Fig. SI-12). A reversible oxidation process is observed at  $E_{1/2}^{(0)+} = -0.345$  V (versus Fc<sup>+</sup>/Fc) followed by second quasi-reversible process at  $E_{1/2}^{(+2+)} = 0.441$  V (versus Fc<sup>+</sup>/Fc).  $Os(PCP)_2$  can also be oxidized using ferrocenium hexafluorophosphate in solution to form a stable blue cation (see below). The  $Os(PCP)_2$  complex is more readily oxidized compared to  $[Os(terpy)_2]^{2+}$  derivatives [1]. However, the stability of  $Os(PCP)_2$  in the formal +2 oxidation state



Fig. 3. Process proposed for the racemization of  $\text{Os}(\text{PCP})_2$  through a  $D_{2d}$  transition state.

is in contrast to bis-cyclometalated,  $Os(ppy)_2(bpy)$  (ppy = 2phenylpyridyl; bpy = 2,2'-bipyridyl) [36]. The oxidation potential of the latter complex, which has cis-configured phenyl rings, is ca. 400 mV more cathodic than  $Os(PCP)_2$  and is isolated as an  $Os^{III}$ species. Apparently, the four PPh<sub>2</sub> moieties impart greater stabilization to the metal center than four pyridyl groups, even in spite the unfavorable trans configuration of the metalated aryl rings in  $Os(PCP)_2$ .

# 3.5. Electronic spectroscopy

Absorption and emission spectra for Os(PCP)<sub>2</sub> are shown in Fig. 4, and photophysical data are listed in Table SI-2. The complex displays strong absorption at 250 nm that gradually diminishes into weaker transitions down to 450 nm ( $\lambda_{max}$  = 335 nm,  $\varepsilon = 2700 \text{ Lmol}^{-1} \text{ cm}^{-1}$ , and  $\lambda_{\text{max}} = 384 \text{ nm}$ ,  $\varepsilon = 1800 \text{ Lmol}^{-1} \text{ cm}^{-1}$ ). Absorption from 250 to 300 nm is assigned to ligand based  $(\pi \rightarrow \pi^*)$  transitions on the basis of a similar intense absorbance found in the PCP-H ligand precursor. The bands at lower energy are assigned to charge transfer transitions (CT) since they are absent in the free ligand (Fig. SI-13). The extinction coefficients for the CT transitions are comparable to values found in other osmium (II) complexes, but are relatively weak when compared to related iridium (III) complexes [26,37]. Upon oxidation with ferrocenium ion the CT transitions undergo a small blue shift that is accompanied by a concomitant appearance of broad transitions the cation  $(\lambda_{\text{max}} = 519 \text{ nm}, \epsilon = 450 \text{ L mol}^{-1} \text{ cm}^{-1}$ for and  $\lambda_{\text{max}} = 591 \text{ nm}, \epsilon = 480 \text{ L mol}^{-1} \text{ cm}^{-1}$ ; Fig. SI-14).

The Os(PCP)<sub>2</sub> complex is non-emissive in fluid solution or when doped (10%) in a PMMA matrix at room temperature. However, a broad, featureless emission ( $\lambda_{max}$  = 546 nm) is observed (quantum yield  $\Phi$  = 0.6) in a dilute solution of 2-MeTHF at 77 K (Fig. 4) with a



**Fig. 4.** Absorption spectrum of  $Os(PCP)_2$  in  $CH_2Cl_2$  solution (black line) and the relative oscillator strengths calculated using TD-DFT (green lines) along with emission spectra recorded in 2-MeTHF glass at 77 K (blue line) and as a neat solid at room temperature (red dashed line). (Color online.)

microsecond lifetime ( $\tau = 8.0 \,\mu s$ ) indicative of phosphorescence. The radiative rate constant is of  $7 \times 10^4 \text{ s}^{-1}$ , and the non-radiative rate constant is  $5 \times 10^4 \text{ s}^{-1}$ . The phosphorescence is at lower energy than that observed from free PCP-H under the same conditions ( $\lambda_{max}$  = 426 nm,  $\tau$  = 1.0 s) [38]. The Os(PCP)<sub>2</sub> complex is also luminescent as a neat solid at room temperature ( $\lambda_{max}$  = 556 nm). The quantum yield ( $\Phi$  = 0.03) and lifetime ( $\tau$  = 0.3 µs, 63%; 2.0 µs, 37%) in the solid state lead to an estimated radiative rate constant of ca.  $3 \times 10^4$  s<sup>-1</sup>, while the non-radiative rate is two orders of magnitudes larger. Cooling the solid to 77 K decreases non-radiative decay. However, the measured lifetimes ( $\tau = 2.2 \,\mu s$ , 38%; 6.3 μs, 62%) indicate that the emission efficiency is less than unity. The biexponential decay is likely due to a combination of molecular and aggregate emission in the solid state. Discussion of the nature of the emissive state will follow from an analysis of the computational studies for  $Os(PCP)_2$ .

#### 3.6. DFT calculations

The electronic structure of Os(PCP)<sub>2</sub> was investigated using density functional theory (DFT) and time-dependent (TD-DFT) methods starting from coordinates of the single crystal structure. Bond lengths within the coordination sphere calculated for Os(PCP)<sub>2</sub> in the gas-phase are slightly longer than values in the crystal structure. The frontier orbitals are shown in Fig. 5. The HOMO and HOMO-1 of Os(PCP)<sub>2</sub> are near degenerate and predominantly localized on the Os center (46%, 38%) and xylyl (L, 31%, 29%), with the remaining contribution from the PPh<sub>2</sub> substituents (L'). The LUMO, LUMO + 1 and LUMO + 2 are also near degenerate and are localized on L' with varying participation from Os. For example, the LUMO has 3% contribution from Os, whereas the amount is 14% for the LUMO + 1 and 2% for LUMO + 2. TD-DFT calculations were used to determine the  $S_0 \rightarrow S_n$  and  $S_0 \rightarrow T_n$  transition energies and oscillator strengths (f) of  $Os(PCP)_2$ . The  $S_0 \rightarrow S_1$ transition calculated for  $Os(PCP)_2$  ( $\lambda = 441$  nm, f = 0.0193) is close to the onset in the experimental absorption spectrum (Table SI-3). Poor overlap between the frontier orbitals of Os(PCP)<sub>2</sub> leads to the small oscillator strength. The  $S_0 \rightarrow S_1$  transition primarily involves HOMO  $\rightarrow$  LUMO + 1 (94%) mixed with higher HOMO  $\rightarrow$ LUMO + 10 (2%) and HOMO  $\rightarrow$  LUMO + 20 (4%) configurations. The LUMO + 10 and LUMO + 20 are primarily metal-centered (MC) and have substantial contributions (3% and 20%, respectively) from antibonding orbitals on Os. On the basis of orbital parentage, the  $S_0 \rightarrow S_1$  transition can be described as principally a metal-xylyl (ML) to PPh<sub>2</sub> (L') charge transfer transition (ML-L'CT) configurationally mixed with metal centered (<sup>1</sup>MC) transitions. The other lowest  $S_0 \rightarrow S_n$  (*n* = 2–10) transitions are all similarly dominated by the ML-L'CT transitions mixed with varying amounts of <sup>1</sup>MC transitions. Likewise, the  $S_0 \rightarrow T_1$  transition ( $\lambda = 491$  nm) involves HOMO  $\rightarrow$  LUMO + 1 (78%) with notable participation from HOMO  $\rightarrow$  LUMO + 20 (16%). DFT calculation of the geometry optimized triplet state gives a self-consistent field ( $\Delta$ SCF) energy separation between  $S_0$  and  $T_1$  that is in good agreement with the emission energy ( $\Delta$ SCF = 2.42 eV,  $\lambda$  = 512 nm). The spin density surface for this state is predominantly localized on the osmium center (65%) with an obvious contribution from the  $d_{(x2-y2)}$  orbital (Fig. 6). The Os–P bonds are elongated (2.53 Å) compared to values in the optimized singlet ground state (2.41 Å), whereas the Os-C bond lengths are little changed. The contribution from the PCP ligand is relatively small, which suggests that the emission from Os(PCP)<sub>2</sub> is dominated by the <sup>3</sup>MC state.

The results from the DFT calculations can be used to construct a qualitative potential energy diagram illustrating surfaces for lowest singlet and triplet states of  $Os(PCP)_2$  (Fig. 7). The lowest singlet state (S<sub>1</sub>) is ML-L'CT in character with a small contribution from the higher lying <sup>1</sup>MC states. The large spin–orbit coupling



**Fig. 5.** Frontier orbitals involved in the  $S_0 \rightarrow S_n$  (n = 1-6) and  $S_0 \rightarrow T_1$  transitions of Os(PCP)<sub>2</sub>.



Fig. 6. Spin density surface calculated for the triplet state of Os(PCP)<sub>2</sub>.



**Fig. 7.** Energy diagram illustrating the radiative and non-radiative decay channels involving the singlet and triplet states of Os(PCP)<sub>2</sub>.

constant of osmium leads to effective intersystem crossing to a triplet state with an increased MC character. The high triplet energy of the PCP ligand favors such mixing between the <sup>3</sup>ML-L'/CT and <sup>3</sup>MC states. Any further elongation of the Os–P bond will increase participation from the <sup>3</sup>MC state. The T<sub>1</sub> state can then readily undergo non-radiative deactivation to the ground state, either vibronically or through a surface crossing, leading to the

rather low quantum yield for the solid state  $Os(PCP)_2$  at room temperature. The quantum yield of the complex is less than unity even at 77 K due to the domination from the <sup>3</sup>MC state, indicating that the barrier to thermal crossing into the <sup>3</sup>MC state is shallow.

It has been widely accepted that the weak emission of  $[Ru(terpy)_2]^{2+}$  at room temperature was due to the thermally activated crossing from the lowest triplet MLCT state to a short-lived <sup>3</sup>MC state, which then undergoes a non-radiative relaxation to the ground state [1]. Recent computational studies on [Ru(terpy)<sub>2</sub>]<sup>2+</sup> show that dissociation of Ru–N bonds is the primary pathway for non-radiative decay [39]. The low temperature (77 K) emission of  $[Ru(terpy)_2]^{2+}$  ( $\lambda_{0-0} = 598$  nm,  $\Phi = 0.48$ ) is from <sup>3</sup>MLCT of low energy level compared with the  $Os(PCP)_2$  complex. The <sup>3</sup>MC state of  $[Ru(terpy)_2]^{2+}$  is inaccessible at 77 K. The related [Os(terpy)<sub>2</sub>]<sup>2+</sup> complexes showed relatively stronger and long-lived luminescence ( $\lambda_{0-0}$  = 714 nm,  $\Phi$  = 0.01) even in solution and at room temperature because the complexes has even lower <sup>3</sup>MLCT, and larger <sup>3</sup>MLCT/<sup>3</sup>MC energy gaps due to the stronger ligand field of osmium. The low temperature (77 K) emission of  $[Os(terpy)_2]^{2+1}$  $(\lambda_{0-0} = 689 \text{ nm}, \Phi = 0.12)$  is of <sup>3</sup>MLCT character. On contrary, emissions at room temperature and low temperature (77 K) observed of complex Os(PCP)<sub>2</sub> are dominated by <sup>3</sup>MC state. The PCP-H ligand is of much higher triplet energy than terpy, and pushes up the <sup>3</sup>MLCT state of Os(PCP)<sub>2</sub> significantly. However, the PCP-H as a poor donor ligand only weakly destabilizes the ligand field of Os(II), and the <sup>3</sup>MC state is accessible at both room temperature and low temperature (77 K). It is noteworthy that emission at 77 K from Os(PCP)<sub>2</sub> is much brighter than that from  $[Ru(terpy)_2]^{2+}$  and  $[Os(terpy)_2]^{2+}$ even though it originates from a <sup>3</sup>MC state. Apparently nonradiative decay is greatly suppressed at 77 K.

# 4. Conclusion

In summary, we have demonstrated the synthetic routes and characterization of the bis-pincer organometallic osmium complex  $Os(PCP)_2$ .  $\Delta$  and  $\Lambda$  enantiomers of  $Os(PCP)_2$  undergo relatively slow exchange processes that can be observed on the NMR time scale. As expected, the poorly conjugated pincer chelate greatly increases the energy of metal and ligand based unoccupied orbitals of the complex  $Os(PCP)_2$ . The large spin–orbit coupling constant of the Os eventually leads to a lowest triplet state with significant amount of metal character, rather than dominant ligand contributions of our initial prediction. The consequence of this is that the

metal centered emission is yellow, rather than blue or violet, which would have been expected if the excited state had more ligand character. Solid  $Os(PCP)_2$  takes advantage of the stable coordination pattern of PCP pincer ligand and displays a 3% quantum yield dominated by the <sup>3</sup>MC state. The non-radiative rate of  $Os(PCP)_2$  is much higher than the radiative rate due to the dissociative character of the metal centered state. The PCP ligand can be viewed as composed of the weaker field ligand diphenyl-phosphine and the stronger field ligand of xylyls. Even though the xylyl phenyls destabilize the metal centered ligand field state to some extent, the metal centered state is still accessible. Another non-radiative channel is also induced by racemization between the two  $Os(PCP)_2$  enantiomers. This non-radiative decay pathway is suppressed when the complex is in a frozen solution and also in the solid state.

# Acknowledgements

This work is sponsored by Universal Display Corporation and NSF CRIF grant 1048807 (X-ray Crystallography). We are grateful to Dr. Travis J. Williams, Dr. Allan Kershaw, graduate students Xinping Wu and Jeff A. Celaje for important discussions and technical assistance with the NMR studies.

#### Appendix A. Supplementary data

CCDC 1000470; contains the supplementary crystallographic data for Os(PCP)<sub>2</sub>. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.poly.2014.06.051.

#### References

- [1] Ruthenium(II) and Osmium(II) Bis(Terpyridine) Complexes in Covalently-Linked Multicomponent Systems: Synthesis, Electrochemical Behavior, Absorption Spectra, and Photochemical and Photophysical Properties J.P. Sauvage, J.-P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola, L. Flamigni, Chem. Rev. 94 (1994) 993.
- [2] Electronic energy transfer and collection in luminescent molecular rods containing ruthenium(II) and osmium(II) 2,2':6',2"-terpyridine complexes linked by thiophene-2,5-diyl spacers S. Encinas, L. Flamigni, F. Barigelletti, E.C. Constable, C.E. Housecroft, E.R. Schoffeld, E. Figgemeier, D. Fenske, M. Neuburger, J.G. Vos, M. Zehnder, Chem. Eur. J. 8 (2002) 137.
- [3] Alkynyl-Bridged Ruthenium(II) 4 '-Diferroceny1-2,2':6',2"-terpyridine electron transfer complexes: synthesis, structures, and electrochemical and spectroscopic studies K.Q. Wu, J. Guo, J.F. Yan, L.L. Xie, F.B. Xu, S. Bai, P. Nockemann, Y.F. Yuan, Organometallics 30 (2011) 3504.
- [4] Characterization of low energy charge transfer transitions in (terpyridine)(bipyridine)Ruthenium(II) complexes and their cyanide-bridged Bi- and Tri-metallic analogues C.N. Tsai, M.M. Allard, R.L. Lord, D.W. Luo, Y.J. Chen, H.B. Schlegel, J.F. Endicott, Inorg Chem 50 (2011) 11965.
- [5] Molecular conductance switch-on of single ruthenium complex molecules K. Seo, A.V. Konchenko, J. Lee, G.S. Bang, H. Lee, J. Am. Chem. Soc 130 (2008) 2553.
- [6] Intramolecular energy-transfer processes in a bis(porphyrin)-ruthenium(II) bis(2,2/: 6',2"-terpyridine) molecular array A.C. Benniston, A. Harriman, C. Pariani, C.A. Sams, Phys. Chem. Chem. Phys. 8 (2006) 2051.
- [7] Dinuclear transition-metal terpyridine complexes with a dithienylcyclopentene bridge directed toward molecular electronic applications Y.W. Zhong, N. Vila, J.C. Henderson, S. Flores-Torres, H.D. Abruna, Inorg. Chem. 46 (2007) 10470.
- [8] Switching of conductance in a molecular wire: role of junction geometry, interfacial distance, and conformational change K.B. Dhungana, S. Mandal, R. Pati, J. Phys. Chem. C 116 (2012) 17268.
- [9] Self-assembled light-harvesting systems: Ru(II) complexes assembled about Rh-Rh cores M.W. Cooke, G.S. Hanan, F. Loiseau, S. Campagna, M. Watanabe, Y. Tanaka, J. Am. Chem. Soc. 129 (2007) 10479.
- [10] Molecular wire type behavior of polycationic multinuclear rack-type Ru-II complexes of polytopic hydrazone-based ligands F. Loiseau, F. Nastasi, A.M. Stadler, S. Campagna, J.M. Lehn, Angew. Chem., Int. Ed. 46 (2007) 6144.
- [11] In search of ruthenium(II) complexes based on tridentate polypyridine ligands that feature long-lived room-temperature luminescence: The

multichromophore approach R. Passalacqua, F. Loiseau, S. Campagna, Y.Q. Fang, G.S. Hanan, Angew. Chem., Int. Ed. 42 (2003) 1608.

- [12] Synthesis of Ru(II) complexes of N-heterocyclic carbenes and their promising photoluminescence properties in water S.U. Son, K.H. Park, Y.S. Lee, B.Y. Kim, C.H. Choi, M.S. Lah, Y.H. Jang, D.J. Jang, Y.K. Chung, Inorg. Chem. 43 (2004) 6896.
- [13] Electronic and geometrical manipulation of the excited state of bis-terdentate homo- and heteroleptic ruthenium complexes J. Dinda, S. Liatard, J. Chauvin, D. Jouvenot, F. Loiseau, Dalton Trans. 40 (2011) 3683.
- [14] A heteroleptic Bis(tridentate) Ruthenium(II) complex of a click-derived abnormal carbene pincer ligand with potential for photosensitzer application B. Schulze, D. Escudero, C. Friebe, R. Siebert, H. Gorls, U. Kohn, E. Altuntas, A. Baumgaertel, M.D. Hager, A. Winter, B. Dietzek, J. Popp, L. Gonzalez, U.S. Schubert, Chem. Eur. J. 17 (2011) 5494.
- [15] Bis(tridentate) ruthenium-terpyridine complexes featuring microsecond excited-state lifetimes D.G. Brown, N. Sanguantrakun, B. Schulze, U.S. Schubert, C.P. Berlinguette, J. Am. Chem. Soc. 134 (2012) 12354.
- [16] Red phosphorescence in Ru-II complexes of a tridentate N-heterocyclic carbene ligand incorporating tetrahydropyrimidine V. Friese, S. Nag, J.H. Wang, M.P. Santoni, A. Rodrigue-Witchel, G.S. Hanan, F. Schaper, Eur. J. Inorg. Chem. 39 (2011).
- [17] Ru(II) complexes with N-heterocyclic carbene ligands or terpyridine analogues: synthesis, characterization, and electrochemical and protondependent spectrometric properties H.J. Park, Y.K. Chung, Dalton Trans 41 (2012) 5678.
- [18] Proton-sensitive luminescent ruthenium(ii) complexes with pyrazine-based pincer-type N-heterocyclic carbene ligands C.S. Lee, R.R. Zhuang, J.C. Wang, W.S. Hwang, I.J.B. Lin, Organometallics 31 (2012) 4980.
- [19] Unsymmetric Ru(II) complexes with N-heterocyclic carbene and/or terpyridine ligands: synthesis, characterization, ground- and excited-state electronic structures and their application for DSSC sensitizers H.J. Park, K.H. Kim, S.Y. Choi, H.M. Kim, W.I. Lee, Y.K. Kang, Y.K. Chung, Inorg. Chem. 49 (2010) 7340.
- [20] The coordination chemistry of dipyridylbenzene N-deficient terpyridine or panacea for brightly luminescent metal complexes? J.A.G. Williams, Chem. Soc. Rev. 38 (2009) 1783.
- [21] Transition metal-carbon bonds. 42. Complexes of nickel, palladium, platinum, rhodium and iridium with tridentate ligand 2,6-Bis[(di-Tbutylphosphino)methyl]phenyl C.J. Moulton, B.L. Shaw, J. Chem. Soc., Dalton (1976) 1020.
- [22] Platinum group organometallics based on "Pincer" complexes: sensors, switches, and catalysts M. Albrecht, G. van Koten, Angew. Chem., Int. Ed. 40 (2001) 3750.
- [23] Cyclometalated phosphine-based pincer complexes: mechanistic insight in catalysis, coordination, and bond activation M.E. van der Boom, D. Milstein, Chem. Rev. 103 (2003) 1759.
- [24] Phosphane coordination to magnesium synthesis and structure of bis[ortho,ortho'-bis((dimethylphosphino)methyl)phenyl]magnesium A. Pape, M. Lutz, G. Muller, Angew. Chem., Int. Ed. Engl. 33 (1994) 2281.
- [25] Highly phosphorescent bis-cyclometalated iridium complexes: Synthesis, photophysical characterization, and use in organic light emitting diodes S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H.E. Lee, C. Adachi, P.E. Burrows, S.R. Forrest, M.E. Thompson, J. Am. Chem. Soc. 123 (2001) 4304.
- [26] Synthesis and characterization of facial and meridional tris-cyclometalated iridium(III) complexes A.B. Tamayo, B.D. Alleyne, P.I. Djurovich, S. Lamansky, I. Tsyba, N.N. Ho, R. Bau, M.E. Thompson, J. Am. Chem. Soc. 125 (2003) 7377.
- [27] Temperature dependence of blue phosphorescent cyclometalated Ir(III) complexes T. Sajoto, P.I. Djurovich, A.B. Tamayo, J. Oxgaard, W.A. Goddard, M.E. Thompson, J. Am. Chem. Soc. 131 (2009) 9813.
- [28] Solution structure and dynamics of 5-coordinate D6 complexes P.R. Hoffman, K.G. Caulton, J. Am. Chem. Soc. 97 (1975) 4221.
- [29] An osmium containing benzene analog, Os(Cschchch)(Co)(Pph3)2, carbonyl(5-thioxo-1,3-pentadiene-1,5-Diyl-C1,C5,S)bis(triphenylphosphine)osmium, and its precursors G.P. Elliott, N.M. Mcauley, W.R. Roper, P.A. Shapley, Inorg. Synth. 26 (1989) 184.
- [30] The facile cyclometallation reaction of 1,3-bis[(diphenylphosphino)methyl]benzene H. Rimml, L.M.J. Venanzi, Organomet. Chem. 259 (1983) C6.
- [31] Vinylidene and carbyne complexes derived from the reactions of OsCl(PPh<sub>3</sub>)(PCP) (PCP=2,6-(PPh<sub>2</sub>CH<sub>2</sub>)(2)CsH<sub>3</sub>) with terminal acetylenes T.B. Wen, Y.K. Cheung, J.Z. Yao, W.T. Wong, Z.Y. Zhou, G.C. Jia, Organometallics 19 (2000) 3803.
- [32] Complexes of bis-ortho-cyclometalated bisphosphinoaryl ruthenium(II) cations with neutral meta-bisphosphinoarene ligands containing an agostic C-H center dot center dot center dot Ru interaction P. Dani, M.A.M. Toorneman, G.P.M. van Klink, G. van Koten, Organometallics 19 (2000) 5287.
- [33] Replacement of a cyclometalated terdentate diamino ligand by a phosphorus analogue. Isolation and crystallographic characterization of an intermediate in aryl C–H bond activation in models of dendrimer-bound organometallic catalysts P. Dani, T. Karlen, R.A. Gossage, W.J.J. Smeets, A.L. Spek, G. vanKoten, J. Am. Chem. Soc. 119 (1997) 11317.
- [34] An inversion recovery NMR kinetics experiment T.J. Williams, A.D. Kershaw, V. Li, X.P. Wu, J. Chem. Educ. 88 (2011) 665.
- [35] J. Kaplan, NMR of Chemically Exchanging Systems, Elsevier Science, 2012.
- [36] Cyclometalated [Os(C–N)(x)(N–N)(3–x)](m+) mimetics of tris(2,2'bipyridine)osmium(II): covering a 2 V potential range by known (x = 0, 1)

and new (x = 2, 3) species (C–N = o-2-phenylpyridinato) R. Ceron-Camacho, S. Hernandez, R. Le Lagadec, A.D. Ryabov, Chem. Commun. 47 (2011) 2823.

- [37] Contemporary progresses on neutral, highly emissive Os(II) and Ru(II) complexes Y. Chi, P.T. Chou, Chem. Soc. Rev. 36 (2007) 1421.
- [38] Electronic excited-states of arylphosphine complexes of copper(I) halides D.J. Fife, W.M. Moore, K.W. Morse, Inorg. Chem. 23 (1984) 1545.
  [39] Experimental and computational exploration of ground and excited state properties of highly strained ruthenium terpyridine complexes P.J. Vallett, N.H. Damrauer, J. Phys. Chem. A 2013 (117) (2013) 6489.