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# Phosphorescent, Cyclometalated Cinchophen-Derived Platinum Complexes: Syntheses, Structures, and Electronic Properties

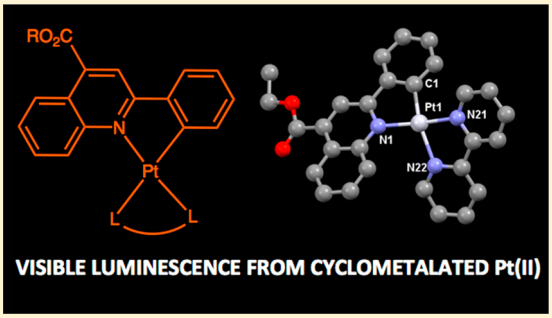
Oliver J. Stacey,[†] James A. Platts,[†] Simon J. Coles,[‡] Peter N. Horton,[‡] and Simon J. A. Pope*[,†]

[†]School of Chemistry, Main Building, Cardiff University, Cardiff CF10 3AT, Cymru/Wales, United Kingdom

[‡]National Crystallographic Service, Chemistry, Faculty of Natural and Environmental Sciences, University of Southampton, Highfield, Southampton, SO17 1 BJ, United Kingdom

Supporting Information

**ABSTRACT:** The syntheses of nine new monometallic heteroleptic platinum complexes [Pt(**L1**−**4**)(acac)], [Pt(**L1**)(hmacac/hfacac)], [PtCl(**L1**)(py)], [Pt(**L1**)(8-Q)], [Pt(**L1**)(bpy)]($PF_6$) (where L1 = 2-phenyl-4-ethyl-quinolinecarboxylate; L2/L3 = *N*-functionalization of 2-phenyl-*N*-aryl/alkyl-quinoline-4-carboxamides; L4 = 2-phenyl-4-quinolinecarboxylic acid (cinchophen); acac = acetylacetonato; hmacac =2,2,6,6-tetramethyl-3,5-heptanedionate; hfacac = hexafluoroacetylacetonate; py = pyridine; 8-Q = 8-quinolinato; bpy =2,2′-bipyridine) are described from precursor dimeric Pt(II) species via an intermediate DMSO adduct of the general form [PtCl(**L1**−**4**)(DMSO)]. Single crystal X-ray diffraction studies were undertaken on three complexes, [Pt(**L1**)(acac)], [PtCl(**L1**)(DMSO)], and [Pt(**L1**)(bpy)]($PF_6$). The structures show that the complexes each adopt a distorted square planar geometry (most severely in the case of [Pt(**L1**)(bpy)]($PF_6$)) with indications of intermolecular Pt−Pt interactions in one example. The complexes were investigated using $^{195}Pt\{^1H\}$ NMR spectroscopy, revealing varied chemical shifts that were strongly dependent upon the specific coordination environment of Pt(II). Luminescence studies showed the complexes possess a phosphorescent character with tunable emission wavelengths between 605 and 641 nm and luminescent lifetimes up to ∼450 ns. Supporting TD-DFT studies provided descriptions of the HOMO and LUMO energy levels of the key complex types, confirming an MLCT contribution to the lowest energy absorption that generally correlated well with the experimental spectra. The contribution of the Pt(5d) center to the calculated HOMOs was strongly ligand dependent, whereas the LUMOs are generally localized over the quinoline component of the cyclometalated ligand.




## INTRODUCTION

Interest in cyclometalated, luminescent Pt(II) complexes has been driven by the potential use of such species in optoelectronic and biological applications.[1] The diversity of applications ultimately lies in the wide range of available ligand systems that can be added to the Pt(II) center in a stepwise manner, determining the overall properties of the complex. For example, resultant square planar complexes have been explored as emitting components of electroluminescent cells,[2] in photocatalysis,[3] as responsive chemosensors to external stimuli (e.g., vapochromism,[4] oxygen sensing[5]), and as luminescent imaging agents[6] for cellular microscopy applications. Reports have also shown that selected complexes can have efficacy as sensitizers for singlet oxygen ($^1O_2$) with subsequent potential as photooxidants.[7] In all of these areas, it is obviously important to understand how to tune the electronic properties while also retaining control over other physical properties, such as solubility. It is also pertinent to recognize the biological significance of related Pt(II) complexes; innumerable studies have investigated the DNA interactions of various Pt(II) species[8] in the context of anticancer (e.g., cisplatin and its relatively poor selectivity for cancerous over healthy cells) and therapeutic agent development. It is notable that *trans*-substituted Pt(II) complexes (e.g., *trans*-[$PtCl_2$(thiazole)$_2$]) have also shown potential against certain tumors.[9]

The types of cyclometalated ligands that have been explored with Pt(II) is now large with either bi- (e.g., N^C) or terdentate (e.g., N^N^C, N^C^N, C^N^C) systems predominating.[1,10] Of course, the ancillary ligands at Pt(II) can vary widely and therefore contribute toward the control of the physical properties, yielding fundamental studies on the tunability of luminescence from cyclometalated Pt(II) complexes. For example, the use of N^C^N type chelates can give long-lived phosphorescent complexes with high quantum efficiencies, and such features have been exploited in cell imaging studies, which also made use of two-photon excitation pathways.[11] Recent studies have utilized planarized aromatic Pt(II) complexes of 2-phenylpyridine (ppy), which have been explored as targeted agents for binding amyloid $\beta$ peptide.[12] The influences of the Pt complexes on protein aggregation via the inhibition of Cu and Zn peptide complex formation (plaques can form in areas of high Zn

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and Cu concentrations) were proposed as an approach to the study of Alzheimer's disease.

In this Article, we describe the first use of 2-phenyl-4-quinolinecarboxylic acid (cinchophen)-derived ligands as cyclometalating agents for Pt(II). The aim was to understand the coordinating ability of 2-phenyl-4-quinoline variants and deduce the reactivity and properties of the resultant Pt(II) complexes. These species show varied, ligand-modulated photophysical properties with tuning of the resultant electronic properties possible through both the cyclometalated component and the ancillary ligands. Characterization of the nine new Pt(II) complexes includes comprehensive multinuclear NMR studies (including $^{195}$Pt), X-ray crystallography, and a combined experimental/theoretical analysis of the electronic properties.

## EXPERIMENTAL SECTION

All reactions were performed with the use of vacuum line and Schlenk techniques. Reagents were commercial grade and were used without further purification. $^{1}$H NMR spectra were recorded on a Bruker Avance dpx 400 or 250 MHz spectrometer, $^{13}$C{$^{1}$H} NMR spectra on a Joel Eclipse 300 MHz or Bruker Avance dpx 500 MHz spectrometer, and $^{195}$Pt NMR spectra on a Bruker Avance dpx 500 MHz spectrometer and were recorded in $CDCl_3$, $D_2O$, $CD_3CN$, or d$^6$-DMSO solutions. $^{1}$H, $^{13}$C{$^{1}$H}, and $^{195}$Pt NMR chemical shifts ($\delta$) were determined relative to internal tetramethylsilane, $Si(CH_3)_4$, and are given in ppm. Low-resolution mass spectra were obtained by the staff at Cardiff University. High-resolution mass spectra were carried out by the staff at Cardiff University and the EPSRC National Mass Spectrometry Service at Swansea University, U.K. All photophysical data was obtained on a JobinYvon−Horiba Fluorolog-3 spectrometer fitted with a JY TBX picosecond photodetection module in $CHCl_3$, MeCN, MeOH, or $H_2O$ solutions. Emission spectra were uncorrected, and excitation spectra were instrument corrected. The pulsed source was a Nano-LED configured for 295, 372, or 459 nm output operating at 500 kHz or 1 MHz. Luminescence lifetime profiles were obtained using the JobinYvon−Horiba FluoroHub single photon counting module, and the data fits yielded the lifetime values using the provided DAS6 deconvolution software. IR spectra were recorded on an ATR-equipped Shimadzu IRAffinity-1 spectrophotometer. UV−vis data were recorded as solutions on a PerkinElmer Lamda20 spectrophotometer.

**X-ray Crystallography.** *Data Collection and Processing.* Suitable crystals were selected and data collected following a standard method[13] on a Rigaku AFC12 goniometer at 100 K equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E-Superbright molybdenum anode generator with either VHF Varimax optics (70 $\mu$m focus) for [Pt(**L1**)(DMSO)Cl] and [Pt(**L1**)(bpy)]($PF_6$) or HF Varimax optics (100 $\mu$m focus) for [Pt(**L1**)(acac)]. Cell determination and data collection were carried out using CrystalClear.[14] The data reduction, cell refinement, and absorption correction used either CrystalClear[14] for [Pt(**L1**)(DMSO)Cl], [Pt(**L1**)(acac)], and [Pt(**L1**)(bpy)]($PF_6$) or CrystAlisPro[15] for [Pt(**L1**)(acac)] and [Pt(**L1**)(bpy)]($PF_6$). Structure solution and refinement were performed using SHELX programs.[16] CCDC 1055479−1055481 contains supplementary X-ray crystallographic data for [Pt(**L1**)(acac)], [Pt(**L1**)(DMSO)Cl], and [Pt(**L1**)(bpy)]($PF_6$), respectively. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, Union Road, Cambridge, CB2 1EZ; Fax(+44) 1223−336−033 or E-mail: deposit@ccdc.cam.ac.uk.

*DFT Studies.* Nonrelativistic calculations were performed on the Gaussian 09 program.[17] Geometry optimizations were carried out without constraints using the B3LYP functional.[18] The Stuttgart−Dresden basis set was used for the Pt atoms[19] and was invoked with pseudopotentials for the core electrons with a 6-31G(d) basis set for all remaining atoms.[20] TD-DFT studies were performed using the same functional but with 6-31+G(d,p) on all nonmetal atoms and also included a simulated MeCN environment using the polarized continuum model (PCM) approach.[21] For prediction of absorption spectra, the geometry used to calculate orbital and other properties was used without modification. For the prediction of emission energies, however, the triplet state was allowed to relax to its optimal geometry using unrestricted B3LYP in the gas phase prior to solvated TD-DFT.

**Synthesis. HL1** was prepared according to literature methodology.[22] A general procedure for preparing sodium salts of $\beta$-diketonates was based on a literature methodology.[23]

*General Procedure for the Synthesis of 2-Phenyl-4-quinolinecarboxamides.* On the basis of a modified literature methodology,[24] thionyl chloride (excess) was added dropwise to a stirring suspension of 2-phenyl-4-quinolinecarboxylic acid (1.1 equiv) in chloroform (10 mL). The reaction was heated at reflux for 16 h under dinitrogen. The solvent was then removed in vacuo, and the yellow solid was redissolved in chloroform (10 mL) before the selected amine (1.0 equiv) was added dropwise to the stirring solution. Et$N^iPr_2$ (excess) was added dropwise, and the mixture was stirred for 16 h at room temperature under dinitrogen. The solvent was removed in vacuo before being redissolved in dichloromethane (20 mL). The crude mixture was washed with aqueous $NaHCO_3$ (sat. 2 × 20 mL), water (1 × 20 mL), and brine (1 × 20 mL). The organic phase was collected, dried over $MgSO_4$, and filtered before the solvent was removed in vacuo.

*Synthesis of **HL2**.*[24] The title compound was synthesized following the general procedure using 2-phenyl-4-quinolinecarboxylic acid (0.233 g, 0.935 mmol) and *tert*-butylamine (0.062 g, 0.850 mmol). Yield = 0.235 g (91%). $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 8.14 (1H, d, $^{3}J_{HH}$ = 8.0 Hz), 8.10−8.05 (3H, m), 7.75 (1H, s), 7.74−7.70 (1H, m), 7.54−7.47 (4H, m), 6.09 (1H, br. s), 1.56 (9H, s).

*Synthesis of **HL3**.*[24] The title compound was synthesized following the general procedure using 2-phenyl-4-quinolinecarboxylic acid (0.233 g, 0.935 mmol) and 4-fluoroaniline (0.094 g, 0.850 mmol). Yield = 0.250 g, (86%). $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 8.18 (1H, d, $^{3}J_{HH}$ = 8.4 Hz), 8.13 (2H, d, $^{3}J_{HH}$ = 8.0 Hz), 8.10−8.08 (2H, m), 7.90 (1H, s), 7.78−7.72 (3H, m), 7.55−7.48 (4H, m), 7.16−7.11 (2H, m).

**Syntheses of the Complexes.** *General Procedure for the Synthesis of Platinum Dimers [Pt(L)(μ-Cl)]$_2$.* On the basis of a modified literature methodology,[25] a solution of potassium tetrachloroplatinate(II) (1.0 equiv) in water (2 mL) was added to a stirring solution of **HL** (1.0 equiv) in 2-ethoxyethanol (6 mL) under dinitrogen and heated to 80 °C for 16 h in a foil-wrapped flask. Brine (10 mL) was added to the cooled solution, and the resultant precipitate was collected on a sinter, washed with water (2 × 10 mL), and dried. The isolated solid was used without purification.

*Synthesis of [Pt(**L1**)(μ-Cl)]$_2$.* The title compound was synthesized following the general procedure for the synthesis of platinum dimers using potassium tetrachloroplatinate(II) (0.084 g, 0.201 mmol) and **HL1** (0.056 g, 0.201 mmol). Yield = 0.049 g (48%). $^{195}$Pt NMR (107.5 MHz, $CDCl_3$): $\delta_{Pt}$ −3219.

*Synthesis of [Pt(**L2**)(μ-Cl)]$_2$.* The title compound was synthesized following the general procedure for the synthesis of platinum dimers using potassium tetrachloroplatinate(II) (0.261 g, 0.629 mmol) and **HL2** (0.191 g, 0.629 mmol). Yield = 0.265 g (79%).

*Synthesis of [Pt(**L3**)(μ-Cl)]$_2$.* The title compound was synthesized following the general procedure for the synthesis of platinum dimers using potassium tetrachloroplatinate (II) (0.171 g, 0.412 mmol) and **HL3** (0.141 g, 0.412 mmol). Yield = 0.151 g (64%).

*General Procedure for Splitting Platinum Dimers.* On the basis of a modified literature methodology,[26] crude [Pt(**L**)(μ-Cl)]$_2$ was dissolved in a minimum volume of DMSO before being precipitated with brine (10 mL), filtered on a sinter, washed with water (2 × 20 mL), and dried. If required, further purification was achieved using silica column chromatography and a 9:1 mixture of dichloromethane and ethyl acetate.

*Synthesis of [PtCl(**L1**)(DMSO)].* The title compound was synthesized following the general procedure above using [Pt(**L1**)(μ-Cl)]$_2$ (0.049 g, 0.048 mmol). The product obtained was a brown/green solid. Yield = 0.053 g (94%). $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 9.07 (1H, d, $^{3}J_{HH}$ = 8.4 Hz), 8.58 (1H, dd, $^{3}J_{HH}$ = 8.4 Hz, $^{4}J_{HH}$ = 1.2 Hz), 8.40−8.35 (1H, m), 8.29 (1H, s), 7.78−7.74 (1H, m), 7.71−7.68 (1H, m), 7.65−7.61 (1H, m), 7.31−7.25 (2H, m), 4.59 (2H, q, $^{3}J_{HH}$ = 7.2 Hz), 3.67 (6H, s with satellites $^{3}J_{HPt}$ = 22 Hz), 1.53 (3H, t, $^{3}J_{HH}$ = 7.2 Hz). $^{13}$C{$^{1}$H} NMR


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(75.6 MHz, $CDCl_3$): $\delta_C$ 166.5, 165.3, 147.6, 145.7, 143.0, 139.9, 133.9, 130.9, 129.8, 128.6, 128.3, 126.1, 125.5, 125.2, 125.0, 117.6, 62.7, 46.3, 14.4. $^{195}$Pt NMR (107.5 MHz, $CDCl_3$): $\delta_{Pt}$ −3662. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 257 (28100), 293 (20100), 366 (9050) nm. IR (thin film) $\nu_{max}$: 3048, 2976, 2918, 1715, 1597, 1578, 1543, 1514, 1466, 1451, 1397, 1375, 1348, 1292, 1271, 1248, 1233, 1194, 1130, 1018, 758 cm$^{-1}$.

*Synthesis of [PtCl(**L2**)(DMSO)].* The title compound was synthesized following the general procedure for splitting the platinum dimers using [Pt(**L2**)($\mu$-Cl)]$_2$ (0.265 g, 0.249 mmol). The product obtained was a yellow/green solid. Yield = 0.283 g (93%). $^{195}$Pt NMR (107.5 MHz, $CDCl_3$): $\delta_{Pt}$ −3675.

*Synthesis of [PtCl(**L3**)(DMSO)].* The title compound was synthesized following the general procedure for splitting the platinum dimers using [Pt(**L3**)($\mu$-Cl)]$_2$ (0.151 g, 0.132 mmol). The product obtained was a brown/green solid. Yield = 0.156 g (91%). $^{195}$Pt NMR (107.5 MHz, $CDCl_3$): $\delta_{Pt}$ −3673.

*General Procedure for Coordinating β-Diketonates to Platinum Complexes.* On the basis of a modified literature methodology,[27] [PtCl(**L**)(DMSO)] (1 equiv) was dissolved in 3-pentanone (5 mL), to which the β-diketonate (1−10 equiv) was added. The reaction was stirred at room temperature for 16 h under dinitrogen. The solvent was removed in vacuo, and the crude product was dissolved in dichloromethane (10 mL), filtered to remove any insoluble salts, and concentrated to dryness in vacuo. The crude product was purified by column chromatography (silica, dichloromethane) wherein elution of the first yellow band with dichloromethane gave the desired product [Pt(**L**)(acac)].

*Synthesis of [Pt(**L1**)(acac)].* The title compound was synthesized following the general procedure for coordinating β-diketonates to platinum complexes using [PtCl(**L1**)(DMSO)] (0.053 g, 0.091 mmol) and sodium acetylacetonate monohydrate (0.111 g, 0.910 mmol). The product obtained was a dark orange solid. Yield = 0.042 g (81%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 9.59 (1H, dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 0.4 Hz), 8.69 (1H, dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.2 Hz), 8.24 (1H, s), 7.81−7.75 (2H, m), 7.65−7.60 (2H, m), 7.29−7.25 (1H, m), 7.21−7.17 (1H, m), 5.58 (1H, s), 4.56 (2H, q, $^3J_{HH}$ = 7.2 Hz), 2.06 (3H, s), 2.05 (3H, s), 1.52 (3H, t, $^3J_{HH}$ = 7.2 Hz). $^{13}$C{$^1$H} NMR (75.6 MHz, $CDCl_3$): $\delta_C$ 185.7, 184.2, 169.4, 165.7, 149.9, 145.7, 140.3, 137.4, 130.8, 130.0, 129.7, 127.7, 126.9, 125.4, 125.2, 125.1, 124.0, 118.1, 101.8, 62.3, 28.5, 27.2, 14.4. $^{195}$Pt NMR (107.5 MHz, $CDCl_3$): $\delta_{Pt}$ −2765. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 253 (17500), 292 (13900), 300 (14400), 363 (5570), 427 (3720) nm. IR (thin film) $\nu_{max}$: 3115, 3053, 2980, 2920, 1723, 1580, 1541, 1522, 1452, 1393, 1375, 1298, 1267, 1238, 1196, 1146, 1028, 762 cm$^{-1}$.

*Synthesis of [Pt(**L1**)(hmacac)].* The title compound was synthesized following the general procedure for coordinating β-diketonates to platinum complexes using [PtCl(**L1**)(DMSO)] (0.023 g, 0.039 mmol) and sodium 2,2,6,6-tetramethyl-3,5-heptanedionate (hmacac) monohydrate (0.009 g, 0.043 mmol). Yield = 0.024 g (93%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 9.70 (1H, d, $^3J_{HH}$ = 9.2 Hz), 8.71 (1H, dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 0.8 Hz), 8.26 (1H, s), 7.88 (1H, dd (with satellites), $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.8 Hz), 7.81−7.77 (1H, m) 7.67−7.61 (2H, m), 7.32−7.28 (1H, m), 7.23−7.19 (1H, m), 5.94 (1H, s), 4.58 (2H, q, $^3J_{HH}$ = 7.2 Hz), 1.54 (3H, t, $^3J_{HH}$ = 7.2 Hz), 1.35 (9H, s), 1.30 (9H, s). $^{13}$C{$^1$H} NMR (75.6 MHz, $CDCl_3$): $\delta_C$ 195.7, 193.9, 169.5, 165.8, 150.0, 145.8, 141.1, 137.4, 131.0, 130.5, 129.7, 127.7, 127.5, 125.4, 125.1, 125.0, 123.9, 118.1, 92.8, 62.4, 42.3, 41.1, 28.8, 28.6, 14.4. $^{195}$Pt NMR (107.5 MHz, $CDCl_3$): $\delta_{Pt}$ −2733. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 253 (18700), 291 (12300), 301 (13000), 357 (5220), 437 (3610) nm. IR (thin film) $\nu_{max}$: 3117, 3057, 2961, 2924, 2855, 1724, 1601, 1584, 1559, 1549, 1530, 1497, 1462, 1452, 1391, 1357, 1360, 1263, 1238, 1225, 1194, 1144, 1026, 791, 760 cm$^{-1}$.

*Synthesis of [Pt(**L1**)(hfacac)].* The title compound was synthesized following the general procedure for coordinating β-diketonates to platinum complexes using [PtCl(**L1**)(DMSO)] (0.022 g, 0.057 mmol), $Na_2CO_3$ (0.007 g, 0.063 mmol), and hexafluoroacetylacetone (0.013 g, 0.063 mmol). The product obtained was a yellow solid. Yield = 0.036 g, (92%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 8.97 (1H, dd, $^3J_{HH}$ = 9.2 Hz, $^4J_{HH}$ = 0.8 Hz), 8.75 (1H, dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.2 Hz), 7.95 (1H, s), 7.64−7.60 (1H, m), 7.57−7.52 (1H, m), 7.37−7.35 (1H, m), 7.24−7.22 (1H, m), 7.10−7.08 (2H, m), 6.21 (1H, s), 4.55 (2H, q, $^3J_{HH}$ = 7.2 Hz), 1.53 (3H, t, $^3J_{HH}$ = 7.2 Hz). $^{13}$C{$^1$H} NMR (125.8 MHz, $CDCl_3$): $\delta_C$ 184.6, 183.1, 168.4, 163.8, 148.6, 144.5, 142.7, 139.1, 130.1, 128.8, 128.7, 126.3, 125.8, 124.1, 124.0, 123.3, 122.9, 121.6, 115.0, 114.9, 113.3, 100.9, 27.4, 26.1. $^{195}$Pt NMR (107.5 MHz, $CDCl_3$): $\delta_{Pt}$ −2693. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 253 (17700), 293 (12500), 370 (5370), 400 (2930) nm. IR (thin film) $\nu_{max}$: 2934, 2851, 1724, 1624, 1603, 1545, 1466, 1456, 1377, 1350, 1260, 1200, 1146, 1109, 1030, 735 cm$^{-1}$.

*Synthesis of [Pt(**L2**)(acac)].* The title compound was synthesized following the general procedure for coordinating β-diketonates to platinum complexes using [PtCl(**L2**)(DMSO)] (0.050 g, 0.077 mmol) and sodium acetylacetonate monohydrate (0.094 g, 0.770 mmol). The product obtained was a dark yellow solid. Yield = 0.046, (94%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 9.51 (1H, d, $^3J_{HH}$ = 8.0 Hz), 7.95 (1H, d, $^3J_{HH}$ = 8.0 Hz), 7.75−7.61 (3H, m), 7.55−7.42 (2H, m), 7.18−7.03 (2H, m), 5.86 (1H, br s), 5.50 (1H, s), 1.97 (3H, s), 1.96 (3H, s), 1.50 (9H, s). $^{13}$C{$^1$H} NMR (125.8 MHz, $CDCl_3$): $\delta_C$ 184.5, 183.1, 168.8, 165.3, 148.6, 144.8, 144.4, 139.2, 130.0, 129.0, 128.6, 126.2, 125.8, 124.0, 123.9, 123.4, 122.9, 112.9, 100.8, 51.9, 27.9, 27.3, 26.2. $^{195}$Pt NMR (107.5 MHz, $CDCl_3$): $\delta_{Pt}$ −2779. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 258 (28800), 297 (28300), 343 (9200), 360 (6800), 415 (3130) nm. IR (thin film) $\nu_{max}$: 3300, 3057, 2963, 2924, 2853, 1721, 1647, 1595, 1572, 1549, 1516, 1456, 1393, 1366, 1302, 1263, 1219, 1161, 1092, 1028, 793, 762, 733, 702 cm$^{-1}$.

*Synthesis of [Pt(**L3**)(acac)].* The title compound was synthesized following the general procedure for coordinating β-diketonates to platinum complexes using [PtCl(**L3**)(DMSO)] (0.050 g, 0.077 mmol) and sodium acetylacetonate monohydrate (0.094 g, 0.770 mmol). The product obtained was a dark yellow solid. Yield = 0.046, (94%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 9.28 (1H, d, $^3J_{HH}$ = 8.8 Hz), 8.95 (1H, s), 7.86 (1H, d, $^3J_{HH}$ = 8.0 Hz), 7.69−7.66 (2H, m), 7.49−7.45 (2H, m), 7.36−7.31 (2H, m), 7.11−6.98 (4H, m), 6.80−6.76 (1H, m), 5.47 (1H, s), 2.00 (3H, s), 1.81 (3H, s). $^{13}$C{$^1$H} NMR (125.8 MHz, $CDCl_3$): $\delta_C$ 184.6, 183.1, 168.4, 163.8, 148.6, 144.5, 142.7, 139.1, 130.1, 128.8, 128.7, 126.3, 125.8, 124.1, 124.0, 123.3, 122.9, 121.6, 121.5, 115.0, 114.9, 113.3, 100.8, 27.4, 26.1. $^{195}$Pt NMR (107.5 MHz, $CDCl_3$): $\delta_{Pt}$ −2769. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 300 (14860), 342 (9840), 363 (4650), 442 (2170) nm. IR (thin film) $\nu_{max}$: 3262, 3063, 2963, 2924, 2853, 1672, 1655, 1582, 1547, 1522, 1508, 1456, 1404, 1373, 1308, 1260, 1211, 1157, 1090, 1015, 939, 864, 833, 800, 760, 729, 698 cm$^{-1}$.

*Synthesis of [Pt(**L4**)(acac)].* [Pt(**L1**)(acac)] (0.029 g, 0.051 mmol) was dissolved in acetone (5 mL) and potassium hydroxide (1 M, 5 mL) and stirred for 16 h at room temperature under dinitrogen. The acetone was removed in vacuo, and the solution was neutralized with hydrochloric acid (1 M). The water was removed in vacuo, and the solid was dissolved in methanol (5 mL) and filtered to remove inorganic salts. Yield = 0.024 g (87%). $^1$H NMR (400 MHz, $CD_3OD$): $\delta_H$ 9.58 (1H, d, $^3J_{HH}$ = 9.2 Hz), 8.30 (1H, dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.6 Hz), 7.93 (1H, s), 7.73−7.69 (1H, m), 7.65−7.62 (1H, m), 7.58−7.53 (2H, m), 7.13−7.07 (2H, m), 5.48 (1H, s), 2.86 (3H, s), 1.81 (3H, s). $^{13}$C{$^1$H} NMR (125.8 MHz, $CD_3OD$): $\delta_C$ 185.7, 183.9, 172.8, 169.9, 150.2, 149.6, 146.5, 139.1, 130.1, 129.5, 128.5, 127.4, 126.3, 126.0, 124.7, 124.4, 123.4, 113.2, 101.0, 26.9, 25.7. $^{195}$Pt NMR (107.5 MHz, $CD_3OD$): $\delta_{Pt}$ −2781. ES MS found $m/z$ = 541.06 for $[M - H]^-$. UV−vis (MeOH) $\lambda_{max}$ ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 282 (4990), 334 (1850), 348 (1940), 382 (1360) nm. IR (thin film) $\nu_{max}$: 3379, 2963, 2918, 2849, 1659, 1576, 1539, 1520, 1454, 1393, 1360, 1337, 1277, 1024, 764 cm$^{-1}$.

*Synthesis of [Pt(**L1**)(8-Q)].* On the basis of a modified literature methodology,[28] [PtCl(**L1**)(DMSO)] (0.038 g, 0.065 mmol), $Na_2CO_3$ (0.008 g, 0.072 mmol), and 8-hydroxyquinoline (0.010 g, 0.072 mmol) were heated to 100 °C with stirring under dinitrogen in 2-methoxyethanol (5 mL) for 24 h. The product was purified by column chromatography (silica, dichloromethane) and then eluted as the first red band with dichloromethane and dried to yield a dark red solid. Yield = 0.035 g (88%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 9.93 (1H, d, $^3J_{HH}$ = 8.8 Hz), 9.18 (1H, d (with satellites $^3J_{HPt}$ = 44 Hz), $^3J_{HH}$ = 5.2 Hz), 8.66 (1H, dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 0.8 Hz), 8.28 (1H, dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 0.8 Hz), 8.23 (1H, s), 7.94−7.91 (1H, m), 7.67−7.63 (2H, m), 7.56−


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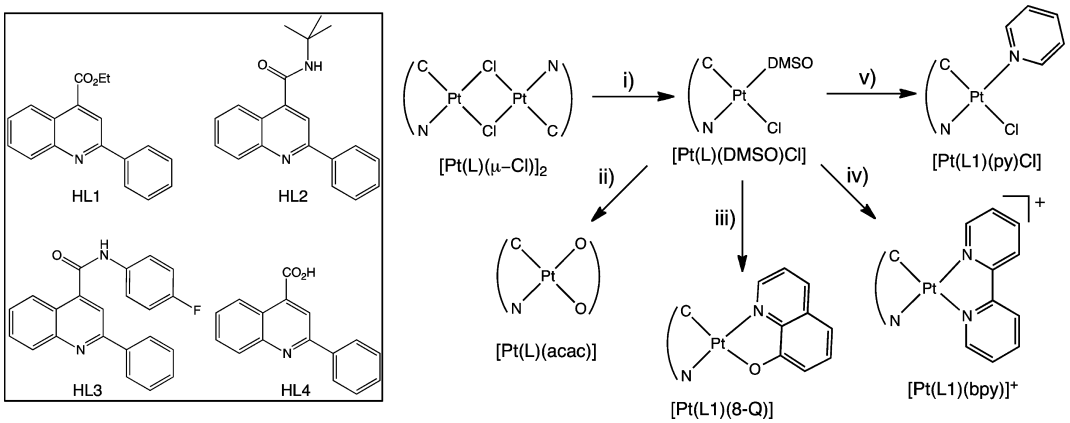
**Scheme 1. Ligands (Inset) and the Reaction Pathways to the Various Cyclometalated Pt(II) Complexes**[a]




[a](i) DMSO, rt; (ii) sodium acac, pentanone, rt; (iii) 8-hydroxyquinoline, 2-methoxyethanol, heat; (iv) 2,2′-bipyridine, DMF, heat; (v) pyridine, acetone, rt.

7.49 (2H, m), 7.40–7.36 (1H, m), 7.28–7.25 (1H, m), 7.22–7.18 (1H, m), 7.15 (1H, dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 0.8 Hz), 6.92 (1H, dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 0.8 Hz), 4.57 (2H, q, $^3J_{HH}$ = 7.2 Hz), 1.53 (3H, t, $^3J_{HH}$ = 7.2 Hz). $^{13}C\{^1H\}$ NMR (75.6 MHz, $CDCl_3$): $\delta_C$ 168.3, 167.4, 165.7, 149.7, 148.1, 147.6, 145.25, 144.66, 138.78, 137.91, 132.90, 131.65, 131.02, 130.83, 129.80, 128.48, 128.0, 125.9, 125.2, 124.7, 123.6, 121.0, 117.9, 116.1, 111.5, 62.4, 14.4. $^{195}$Pt NMR (107.5 MHz, $CDCl_3$): $\delta_{Pt}$ −2922. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 257 (16700), 284 (15900), 370 (12400) nm. IR (thin film) $\nu_{max}$: 3063, 2965, 2934, 2864, 1721, 1653, 1645, 1599, 1580, 1541, 1501, 1452, 1375, 1352, 1294, 1262, 1240, 1196, 1144, 1092, 1084, 1022, 795, 762, 733 cm$^{-1}$.

*Synthesis of [PtCl(**L1**)(py)].* Prepared by a modified literature methodology,[29] pyridine (0.007 g, 0.094 mmol) and [PtCl(**L1**)-(DMSO)] (0.050 g, 0.086 mmol) were dissolved in acetone (5 mL) and stirred for 16 h under dinitrogen at room temperature. The solvent was removed in vacuo, and the product was purified by precipitation from diethyl ether. Yield = 0.043 g (86%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 9.80 (1H, dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 0.8 Hz), 9.01 (2H, d (with satellites $^3J_{HPt}$ = 48.0 Hz)), 8.59 (1H, d, $^3J_{HH}$ = 8.4 Hz), 8.23 (1H, s), 7.93–7.89 (1H, m), 7.83–7.79 (1H, m), 7.67–7.60 (2H, m), 7.47–7.44 (2H, m), 7.19–7.16 (1H, m), 7.03–6.98 (1H, m), 6.29 (1H, dd (with satellites $^3J_{HPt}$ = 42.4 Hz), $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 0.8 Hz), 4.57 (2H, q, $^3J_{HH}$ = 7.2 Hz), 1.52 (3H, t, $^3J_{HH}$ = 7.2 Hz). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): $\delta_C$ 168.1, 165.6, 154.1, 149.3, 146.0, 143.7, 138.5, 138.0, 131.0. 130.6, 130.3, 129.5, 128.1, 126.1, 125.7, 124.9, 124.7, 123.9, 117.6, 62.4, 14.3. $^{195}$Pt NMR (107.5 MHz, $CDCl_3$): $\delta_{Pt}$ −3158. UV−vis ($CHCl_3$) $\lambda_{max}$ ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 255 (31800), 285 (26000), 367 (12800), 450 (1990) nm. IR (thin film) $\nu_{max}$: 3096, 3053, 2980, 2924, 2224, 1723, 1717, 1580, 1541, 1451, 1373, 1292, 1267, 1240, 1196, 1144, 1024, 907, 864, 760, 727, 689 cm$^{-1}$.

*Synthesis of [Pt(**L1**)(bpy)](PF$_6$).* Prepared by a modified literature methodology,[30] 2,2′-bipyridine (0.031 g, 0.200 mmol) and [PtCl(**L1**)-(DMSO)] (0.070 g, 0.182 mmol) were dissoved in dimethylformamide (5 mL) and stirred for 48 h under dinitrogen at 65 °C. Diethyl ether was added to precipitate the complex, which was filtered and washed. The yellow solid was dissolved in acetonitrile before a saturated aqueous solution of potassium hexafluorophosphate was added dropwise. The precipitate was dissolved in dichloromethane before being washed with water (2 × 50 mL), dried over $MgSO_4$, and filtered, and the solvent was reduced in volume. Diethyl ether was added to the precipitate, and the solid was collected by filtration, washed with diethyl ether, and dried to yield a dark yellow solid. Yield = 0.057 g (73%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta_H$ 9.40 (1H, dd $^3J_{HPt}$ = 40.8 Hz, $^3J_{HH}$ = 6.0 Hz), 8.66–8.61 (2H, m), 8.39–8.34 (1H, m), 8.32–8.28 (3H, m), 8.17–8.13 (1H, m), 8.09–8.07 (1H, m), 7.81–7.73 (3H, m), 7.64–7.61 (1H, m), 7.43–7.36 (2H, m), 7.29–7.22 (2H, m), 4.60 (2H, q, $^3J_{HH}$ = 7.2 Hz), 1.53 (3H, t, $^3J_{HH}$ = 7.2 Hz). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CD_3CN$): $\delta_C$ 167.6, 164.9, 157.3, 155.0, 152.8, 150.9, 146.5, 146.1, 142.3, 140.5, 140.1, 140.0, 132.0, 131.3, 130.3, 128.6, 128.2, 127.0, 126.5, 126.3, 125.2, 124.9, 124.6, 124.0, 123.3, 118.1, 62.6, 13.3. $^{195}$Pt NMR (107.5 MHz, $CD_3CN$): $\delta_{Pt}$ −3097. HR MS (ES) found $m/z$ = 627.1365; calculated $m/z$ = 627.1360 for $[C_{28}H_{22}N_3O_2{}^{195}Pt]^+$. UV−vis ($CH_3CN$) $\lambda_{max}$ ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$): 281 (28600), 318 (12900), 355 (10900), 368 (11500), 395 (8200), 448 (2460) nm. IR (thin film) $\nu_{max}$: 3086, 3055, 2984, 2932, 1723, 1669, 1599, 1582, 1545, 1472, 1449, 1377, 1267, 1246, 1200, 1157, 1146, 1024, 839, 762, 731, 700 cm$^{-1}$.

## RESULTS AND DISCUSSION

**Syntheses and Characterization of the Ligands and Complexes.** **HL2** and **HL3** were formed through the reaction of 2-phenylquinoline-4-carbonyl chloride and two commercially available primary amines (*tert*-butylamine and 4-fluoroaniline, respectively) based on a modified literature methodology.[24] The cyclometalated dichloro-bridged dimers, [Pt(**L**)(μ-Cl)]$_2$, were obtained from reactions with potassium tetrachloroplatinate(II) and the corresponding ligand. It is noteworthy that exhaustive attempts at synthesizing the complexes were made using a range of previously reported synthetic methodologies before a suitable reaction route was found. For example, initial attempts utilized 2-methoxyethanol and water (3:1) as solvent at 100 °C for 48 h[31] but yielded a gray, insoluble solid (suggestive of reduced Pt[28]) together with free ligand isolated in near quantitative yield. The conditions outlined by Shavaleev et al.[28] using [$PtCl_4$]($Bu_4N$)$_2$ in ethanol and dichloromethane to circumvent this issue were also not applicable to the systems described here.

A successful experimental procedure involved dropwise addition of tetrachloroplatinate(II) in water to the ligand dissolved in 2-ethoxyethanol.[32] Importantly, the platinate(II) remained dissolved by increasing the overall volume of the reaction solvent while maintaining the 3:1 ratio (typically using 50–100 mg of platinate(II) required 8 mL of solvent). The reaction vessel was flushed with nitrogen and wrapped in foil to prevent photoreduction.[33] The mixtures were then heated to 80 °C for 24–48 h before being cooled to room temperature. The [Pt(**L**)(μ-Cl)]$_2$ products were precipitated using brine to give green/yellow/brown solids upon filtration and used as isolated (Scheme 1).

The dimers were then split with DMSO to give monometallic [PtCl(**L**)(DMSO)] following a preparative method described by Godbert et al.[25] Subsequent purification by flash column chromatography on silica using a 9:1 mixture of dichloromethane and ethyl acetate yielded the products as dark orange solids. The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DMSO adducts were shown to be spectroscopically pure and could therefore be used as isolated after column chromatography.

For the β-diketonate Pt(II) complexes, sodium salts of acetylacetonate (acac) and 2,2,6,6-tetramethyl-3,5-heptanedionate (abbreviated to hexamethylacetylacetonate: hmacac) were utilized,[25] and hexafluoroacetylacetone (hfacac) was used as provided. The [PtCl(**L**)(DMSO)] complexes were dissolved in a small volume (∼5 mL) and reacted with the acac ligands in 3-pentanone. The complexes were again purified by flash column chromatography on silica and were all eluted as the first yellow/orange band using dichloromethane. [Pt(**L4**)(acac)] was synthesized via the base-mediated ester hydrolysis of [Pt(**L1**)-(acac)] in a similar manner to that reported previously.[31]

The complexes were characterized by $^{1}$H, $^{13}$C{$^{1}$H}, and $^{195}$Pt{$^{1}$H} NMR as well as UV−vis and IR spectroscopy and, when amenable, mass spectrometry. $^{1}$H NMR was used to observe both the α-proton on the β-diketonate at ∼5.5 ppm as well as the methyl groups as two very close singlets at ∼2 ppm. $^{3}J_{HPt}$ satellites were discernible at 7.75 ppm for the adjacent proton to the cyclometalated carbon.

The neutral Pt(II) complex, [Pt(**L1**)(8-Q)], was isolated using the methodology reported by Shavaleev et al.[28] The $^{1}$H NMR spectrum was more complex with overlapping aromatic protons, but comparison to the [PtCl(**L**)(DMSO)] spectra revealed a wider range in the aromatic protons with downfield shifts close to 9.9 ppm and upfield shifts to 6.8 ppm. The presence of a second set of satellites at 9.18 ppm relating to $^{3}J_{HPt}$ coupling (Supporting Information (SI), Figure S1) for the proton on C$^{2}$ of the 8-quinolinato ligand also confirmed the proposed coordination sphere.

Reaction of [PtCl(**L1**)(DMSO)] with 2,2′-bipyridine (bpy) gave cationic [Pt(**L1**)(bpy)](PF$_6$) using a similar methodology to the literature, albeit with extended reaction times (up to 72 h).[34] The related compound [PtCl(**L1**)(py)] (py = pyridine) was obtained by reacting the DMSO adduct precursor in acetone with pyridine in slight excess.[29] The $^{1}$H NMR spectrum revealed two equivalent protons with $^{195}$Pt satellites at 9.01 ppm corresponding to the two equivalent protons at the 2,6-positions of pyridine with $^{3}J_{HPt}$ coupling. Interestingly, the proton adjacent to the cyclometalating carbon shifts substantially upfield (6.29 ppm) in comparison to the other analyzed species.

**$^{195}$Pt{$^{1}$H} NMR Studies.** It should be noted that the literature reports of $^{195}$Pt NMR shifts for cyclometalated Pt(II) complexes are relatively limited, possibly due to the limited solubility of such complexes. For the [Pt(**L**)(acac)] (where **L** = **L1**−**4**) complexes, $\delta_{Pt}$ values range from −2765 to −2781 ppm (note the data for [Pt(**L4**)(acac)] was recorded in CD$_3$OD solvent and solvent type can affect the observed shift in $^{195}$Pt NMR), suggesting the varied functionality at the 4-position of the phenylquinoline chelate has very little influence upon the chemical shift of the $^{195}$Pt center;[35] for reference, the related known compound [Pt(ppy)(acac)] (where ppy =2-phenylpyridine) possesses a shift of −2868 ppm,[35] suggesting that coordination of **L1** results in a more deshielded Pt(II) center. However, altering the ancillary β-diketonate ligand induced a much greater change in $\delta_{Pt}$. A shift of almost 100 ppm was observed between acac and hfacac variants due to the contrasting donating ability of the ligands.

Alteration of the ligand donor set induced even greater modulation of $\delta_{Pt}$. For example, [PtCl(**L1**)(DMSO)] has a $^{195}$Pt NMR shift of −3662 ppm, the most upfield shift observed throughout the complexes, which is consistent with the reports on the ppy analogue, which appear at −3351[36] or −3807 ppm.[34] The β-diketonate complexes gave rise to the most deshielded Pt(II) centers and lie around −2770 ppm. [Pt(**L1**)(8-Q)] and [PtCl(**L1**)(py)] lie between these extremes with observed resonances at −2922 and −3158 ppm, respectively. It is noteworthy that [PtCl(ppy)(py)] has a reported shift of −1632 ppm (in d$^6$-acetone), which starkly contrasts to the $\delta_{Pt}$ values reported herein.[36] The cationic [Pt(**L1**)(bpy)](PF$_6$) gave $\delta_{Pt}$ at −3097 ppm, and for completion, the $^{195}$Pt NMR shift for the starting dimeric material [Pt(**L1**)(μ-Cl)]$_2$ (−3219 ppm) was also obtained.

**X-ray Crystallographic Studies.** Three sets of crystals were isolated using vapor diffusion of diethyl ether into concentrated chloroform solutions of the complexes and were found to be suitable for crystallographic studies. The data collection parameters are presented in Table S1 (SI). The crystal structure for [Pt(**L1**)(acac)] (Figure 1) revealed the expected distorted

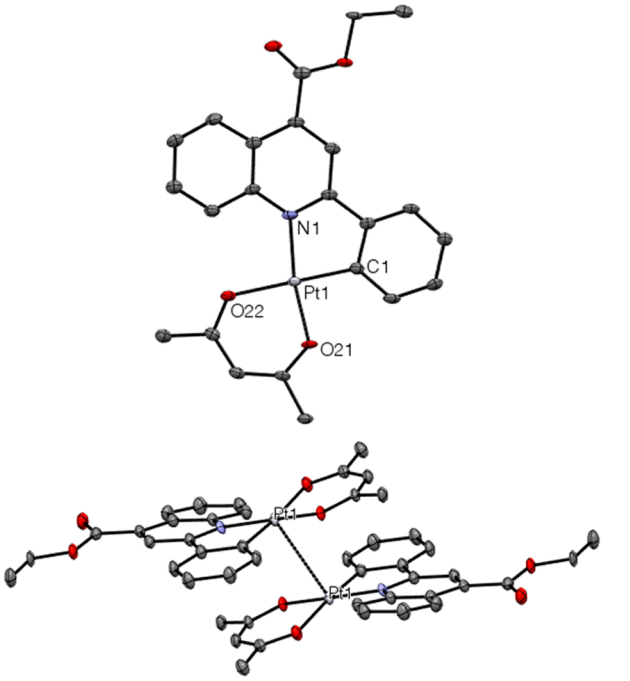


**Figure 1.** X-ray crystal structure of [Pt(**L1**)(acac)] (top) and the Pt−Pt interaction (bottom). Hydrogen atoms omitted for clarity. The ellipsoid probabilities are at 50%.

square planar geometry. The Pt−C bond length was 1.960(4) Å (compared to [Pt(ppy)(acac)] reported at 1.948 Å).[37] The structure of [Pt(ppy)(acac)] has reported metallophilic interactions with a Pt−Pt distance of ∼3.669 Å (well within the van der Waals radius for Pt),[38] and this was also the case for [Pt(**L1**)(acac)], where the Pt−Pt distance was actually shorter at 3.3150(3) Å. Both structures pack in a similar manner with a head-to-tail arrangement whereby the cyclometalated ligand of one molecule lies above or below the ancillary ligand of another. The bond distances between the protons *ortho* to the cyclometalating atoms and the coordinated oxygen atoms in the known ppy species are approximately 2.442 Å (pyridyl) and 2.574 Å (phenyl), whereas the comparable distances in [Pt(**L1**)(acac)] are 2.058(4) Å (pyridyl) and 2.429(3) Å (phenyl). Although the distances on the phenyl side of the molecule are very similar, there is a marked decrease in distance


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on the pyridyl side, even with the increased distance created through 21.1(2)° of torsion.

The crystal structure of [PtCl(**L1**)(DMSO)] (Figure 2) has a very distorted square planar arrangement due to the unfavorable

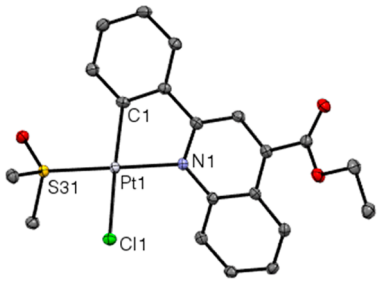


**Figure 2.** X-ray crystal structure of [PtCl(**L1**)(DMSO)]. Hydrogen atoms omitted for clarity. The ellipsoid probabilities are at 50%.

interaction between the proton on the quinoline ring and the coordinated chloride (Pt−Cl at 2.4070(5) Å). The resultant strain induces a twist in the molecule, whereby the S−Pt−Cl plane is at a 43.8(1)° angle to the quinoline ring. There are no Pt−Pt interactions within the crystal packing; the head-to-tail motif still exists, but in this example, the cyclometalated ligand of one molecule sits over the cyclometalated ligand of another, resulting in $\pi-\pi$ interactions but no metallophilic contacts.

The X-ray crystal structure of [Pt(**L1**)(bpy)]($PF_6$) (Figure 3) also displays a high degree of distortion from the square planar

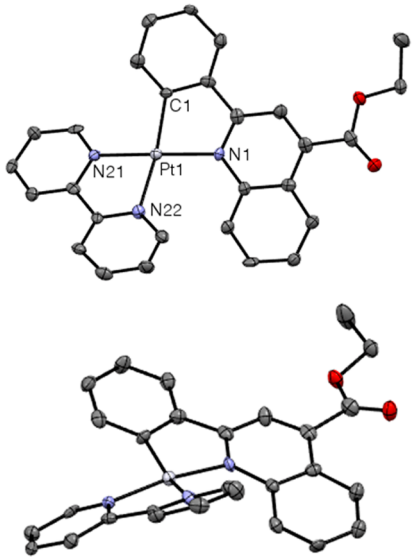


**Figure 3.** X-ray crystal structure of [Pt(**L1**)(bpy)]($PF_6$). Hydrogen atoms and $PF_6^-$ counteranion omitted for clarity. The ellipsoid probabilities are at 50%.

geometry with both the bpy (12.4(3)°) and cyclometalated ligand (5.2(3)°) displaying internal twisting, resulting in a significant angle of 43(1)° between the plane of the bpy and the plane of the cyclometalated ligand due to unfavorable H/H interactions between the two chelating ligands. The distortion accommodates Pt−C and Pt−N distances (2.012(6) Å and 2.022(5)−2.145(5) Å, respectively) that are in the normal range expected for this type of complex (Table 1). Despite this, and unlike [PtCl(**L1**)(DMSO)], a longer Pt−Pt distance was observed at ∼4.3413(5) Å, which is at the limit of interactivity based on the van der Waal's radius calculated for Pt by Alvarez.[38]

**DFT Calculations.** Theoretical calculations revealed that, in all cases, the majority of the electron density in the HOMO lies across both the ancillary ligand and the phenyl moiety of the cyclometalated ligand as well as the d orbitals of the platinum. The orbital representations and the calculated lowest energy HOMO−LUMO transitions are shown in Figure 4 and SI Figure S2 and Table S2. The percent contribution to the energy levels for the Pt(II) 5d orbitals were calculated from the theoretical data and allowed a qualitative assessment of possible LLCT, MLCT, and ILCT transitions to be investigated for each class of compound. Table 2 shows that there is a large variation in the percentage of d orbital character that contributes to the HOMOs and that the nature of the ancillary ligand can strongly modulate this contribution. Calculations on the acac and hfacac species suggest that an admixture of transitions contributes to the visible absorption. For [Pt(**L1**)(8-Q)], the HOMO is predominantly localized on the 8-quinolato ligand and indicative of a strong LLCT transition, whereas for the cationic species [Pt(**L1**)(bpy)]($PF_6$), the HOMO apears to be much more localized over the cyclometalated ligand with the corresponding LUMO distributed across both chelating ligands. Overall, the calculated results predict that very simple changes to the nature of the ancillary ligands and the coordination sphere may alter the relative contribution from Pt(II) 5d orbitals and the HOMO and LUMO distributions.

**Electronic Properties.** The absorption properties of all of the complexes were measured in chloroform except for [Pt(**L4**)(acac)], which was measured in methanol, and [Pt(**L1**)(bpy)]($PF_6$), which was measured in acetonitrile (Figure 5). The spectra all reveal strong absorptions between 250 and 350 nm corresponding to intraligand $^1IL(\pi \rightarrow \pi^*)$ transitions. Lower energy transitions from ∼350 nm, tailing off beyond 500 nm, can be classified as a combination of metal-to-ligand charge transfer ($^1$MLCT) and ligand-to-ligand charge transfer ($^1$LLCT) transitions. Known data for [Pt(ppy)(acac)] and [Pt(ppy)(hfacac)], where the lowest energy absorption maxima lie around 350−370 nm, shows that the observed transitions for the phenylquinoline complexes are bathochromically shifted, presumably due to the extended conjugation of the quinoline unit.[39] Data for previously reported [Pt(pq)(acac)] (pq = phenylquinoline) and [Pt(isoquinoline)(acac)] correlate more closely with low energy transitions at 400−420 nm.[40] Changing functionalization from ester to amide invoked a minor change in the absorption profile, especially around 340−400 nm, whereas altering the substituent (*tert*-butyl versus *para*-fluorobenzene) of the amide had very little influence. However, the visible absorption properties were strongly affected by the nature of the ancillary ligand. For example, the different $\beta$-diketonates induced subtle shifts in the absorption maxima at ∼430−440 nm. Comparison of the absorption spectral profiles with the calculated oscillator strengths (Table S2, SI) reveals good correlation between the theoretical and experimental results, especially in the visible region associated with the putative $^1$MLCT and $^1$LLCT transitions.

Steady state luminescence and lifetime data (Table 3) were acquired for the majority of complexes using aerated chloroform. Cationic [Pt(**L1**)(bpy)]($PF_6$) was studied as an acetonitrile solution, and the hydrophilic nature of [Pt(**L4**)(acac)] facilitated studies in methanol and water. All complexes were shown to be visibly emissive with a broad, unstructured peak around 605−641 nm with corresponding lifetimes in the range of 182−427 ns for


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**Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) from the Crystallographic Data**

| [Pt(**L1**)(acac)] | | [PtCl(**L1**)(DMSO)] | | [Pt(**L1**)(bpy)](PF$_6$) | |
|---|---|---|---|---|---|
| Bond Lengths (Å) | | | | | |
| Pt(1)−C(1) | 1.960(4) | Pt(1)−C(1) | 2.010(2) | Pt(1)−C(1) | 2.012(6) |
| Pt(1)−O(21) | 1.999(3) | Pt(1)−Cl(21) | 2.4070(5) | Pt(1)−N(21) | 2.022(5) |
| Pt(1)−N(1) | 2.045(3) | Pt(1)−N(1) | 2.0788(19) | Pt(1)−N(1) | 2.046(5) |
| Pt(1)−O(22) | 2.101(3) | Pt(1)−S(31) | 2.2184(6) | Pt(1)−N(22) | 2.145(5) |
| Bond Angles (deg) | | | | | |
| C(1)−Pt(1)−O(21) | 89.32(14) | C(1)−Pt(1)−N(1) | 80.66(9) | C(1)−Pt(1)−N(21) | 99.7(2) |
| C(1)−Pt(1)−N(1) | 81.11(15) | C(1)−Pt(1)−S(31) | 98.35(7) | C(1)−Pt(1)−N(1) | 80.4(2) |
| O(21)−Pt(1)−N(1) | 169.89(12) | N(1)−Pt(1)−S(31) | 174.62(5) | N(21)−Pt(1)−N(1) | 169.3(2) |
| C(1)−Pt(1)−O(22) | 173.87(12) | C(1)−Pt(1)−Cl(1) | 160.43(7) | C(1)−Pt(1)−N(22) | 157.3(2) |
| O(21)−Pt(1)−O(22) | 89.24(11) | N(1)−Pt(1)−Cl(1) | 94.00(6) | N(21)−Pt(1)−N(22) | 77.7(2) |
| N(1)−Pt(1)−O(22) | 99.94(12) | S(31)−Pt(1)−Cl(1) | 88.63(2) | N(1)−Pt(1)−N(22) | 106.3(2) |

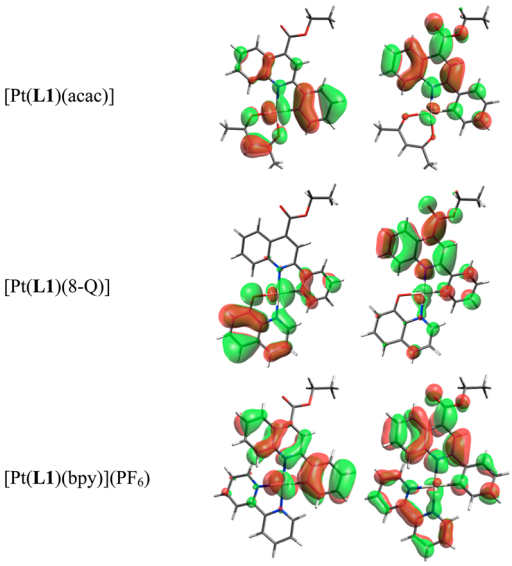


**Figure 4.** Calculated representations of HOMO (left) and LUMO (right) for selected complexes.

**Table 2. Percentage Pt 5d Orbital Character Predicted for the HOMO-2, HOMO-1, HOMO, and LUMO for Selected Complexes**

| | Pt 5d orbital character (%) | | | |
|---|---|---|---|---|
| compound | HOMO-2 | HOMO-1 | HOMO | LUMO |
| [Pt(**L1**)(acac)] | 41.81 | 35.51 | 40.29 | 2.00 |
| [Pt(**L1**)(hfacac)] | 37.52 | 19.01 | 24.83 | 0.96 |
| [PtCl(**L1**)(DMSO)] | 11.54 | 16.38 | 23.29 | 0.32 |
| [Pt(**L1**)(py)Cl] | 7.10 | 11.25 | 26.48 | 1.00 |
| [Pt(**L1**)(8-Q)] | 31.13 | 14.12 | 4.25 | 0.47 |
| [Pt(**L1**)(bpy)](PF$_6$) | 15.54 | 24.88 | 6.47 | 0.25 |

the acacs and 59−365 ns for the other variants (e.g., Figure 6). It is noteworthy that the authentic cinchophen complex, [Pt(**L4**)(acac)], retained these advantageous visible emission characteristics in aqueous solution. Quantum yield measurements on a selection of complexes in aerated solvent ranged between 0.04 and 0.46%. These observations are consistent with an emission that comprises significant $^3$MLCT character at room temperature. The lack of vibronic structure to the emission profile, as noted for a number of other N^C cyclometalated Pt(II) complexes,[10] suggests that there is little mixing of $^3$LC and $^3$MLCT states.

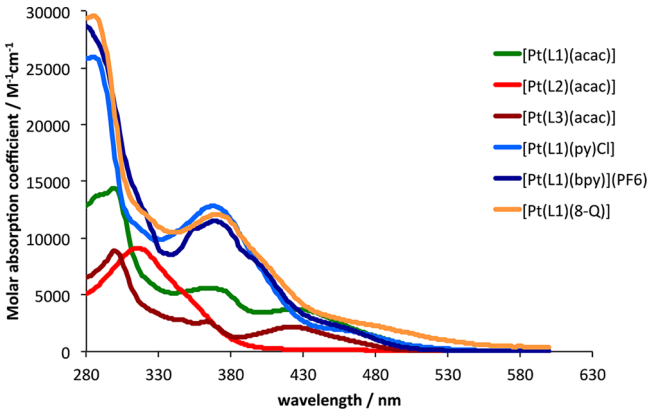


**Figure 5.** UV−vis absorption profiles for selected complexes in solution (all measured in $CHCl_3$ except [Pt(**L1**)(bpy)](PF$_6$) in MeCN).

**Table 3. UV−Vis and Luminescence Properties of the Complexes**

| compound[a] | $\lambda_{abs}$ (nm) | $\lambda_{em}$ (nm)[e] | $\tau$ (ns)[f] |
|---|---|---|---|
| [Pt(**L1**)(acac)] | 253, 292, 300, 363, 427 | 639 | 331 |
| [Pt(**L2**)(acac)] | 258, 297, 343, 360, 415 | 615 | 427 |
| [Pt(**L3**)(acac)] | 300, 342, 363, 442 | 629 | 368 |
| [Pt(**L4**)(acac)] | 282, 334, 348, 382[b] | 605,[b] 605[c] | 249,[b] 182[c] |
| [Pt(**L1**)(hmacac)] | 253, 291, 301, 357, 437 | 641 | 318 |
| [Pt(**L1**)(hfacac)] | 253, 293, 370, 400, 442 | 616 | 262 |
| [PtCl(**L1**)(DMSO)] | 257, 293, 366, 420 | 610 | 113 |
| [PtCl(**L1**)(py)] | 255, 285, 367, 450 | 626 | 365 |
| [Pt(**L1**)(8-HQ)] | 257, 284, 370, 455 | 620 | 59 |
| [Pt(**L1**)(bpy)](PF$_6$) | 281, 318, 355, 368, 395, 448[d] | 630[d] | 155[d] |

[a]In chloroform unless stated otherwise. [b]In methanol. [c]In water. [d]In acetonitrile. [e]$\lambda_{exc}$ = 425 nm. [f]$\lambda_{exc}$ = 372 nm.

The emission character was moderately dependent on the specific nature of the complex, the results revealing that alteration of the ancillary ligand, and the substitution of the phenylquinoline ligand, both allow effective tuning of the emission maxima of these cyclometalated Pt(II) complexes. For the acac complexes, altering the functionality of the $\beta$-diketonate clearly influences both the lifetime and emission wavelength with [Pt(**L1**)(hmacac)] possessing the most bathochromically shifted luminescence maximum.

In summary, we have presented a general synthetic route to isolating a range of new cyclometalated Pt(II) complexes based upon chelated cinchophen-derived ligands. X-ray crystallo-


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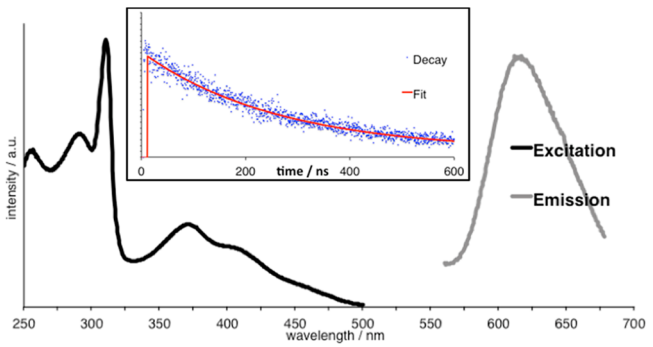


**Figure 6.** Excitation ($\lambda_{em}$ = 615 nm) and emission ($\lambda_{ex}$ = 425 nm) spectra for [Pt(**L1**)(hfacac)] ($\lambda_{ex}$ = 425 nm). (inset) Fitted ($\tau$ = 262 ns) monoexponential decay profile for [Pt(**L1**)(hfacac)] ($\lambda_{ex}$ = 372 nm).

graphic studies have confirmed the square planar structures of three examples, including a key DMSO-adduct intermediate, [PtCl(**L1**)(DMSO)], and a highly distorted cationic diimine complex, [Pt(**L1**)(bpy)]($PF_6$). A combined theoretical and experimental investigation of the electronic properties revealed that a likely admixture of MLCT and LLCT character dominates the visible absorption characteristics; the tunable luminescence of the complexes was attributed to significant $^3$MLCT character. The varied functionality of the complexes was also exploited to broaden the choice of solvents for the photophysical measurements, allowing aqueous emission to be demonstrated for [Pt(**L4**)(acac)]. In conclusion, cinchophen (2-phenyl-4-quinolinecarboxylic acid) provides an excellent ligand base for accessing stable Pt(II) complexes with tunable luminescence properties.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

X-ray crystallographic data of [Pt(**L1**)(acac)], [PtCl(**L1**)(DMSO)], and [Pt(**L1**)(bpy)]($PF_6$) in CIF format. Parameters associated with the single crystal diffraction data collection, selected NMR spectra, and TD-DFT calculated orbital representations. This material is free of charge via the Internet at The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00817.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail: popesj@cardiff.ac.uk.

### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

(1) (a) Williams, J. A. G.; Develay, S.; Rochester, D. L.; Murphy, L. *Coord. Chem. Rev.* **2008**, *252*, 2596−2611. (b) Diez, A.; Lalinde, E.; Teresa Moreno, M. *Coord. Chem. Rev.* **2011**, *255*, 2426. (c) Prokhorov, A. M.; Hofbeck, T.; Czerwieniec, R.; Suleymanova, A. F.; Kozhevnikov, D. N.; Yersin, H. *J. Am. Chem. Soc.* **2014**, *136*, 9637−9642.

(2) (a) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 151. (b) Kwong, R. C.; Sibley, S.; Dubovoy, T.; Baldo, M. A.; Forrest, S. R.; Thompson, M. E. *Chem. Mater.* **1999**, *11*, 3709−3713. (c) O'Brien, D. F.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, *74*, 442−444.

(3) (a) Houlding, V. H.; Frank, A. J. *Inorg. Chem.* **1985**, *24*, 3664−3668. (b) Maruyama, T.; Yamamoto, T. *J. Phys. Chem. B* **1997**, *101*, 3806−3810.

(4) (a) Grove, L. J.; Rennekamp, J. M.; Jude, H.; Connick, W. B. *J. Am. Chem. Soc.* **2004**, *126*, 1594−1595. (b) Zhang, X.; Wang, J.-Y.; Ni, J.; Zhang, L.-Y.; Chen, Z.-N. *Inorg. Chem.* **2012**, *51*, 5569−5579. (c) Ni, J.; Wang, Y.-G.; Wang, J.-Y.; Zhao, Y.-Q.; Pan, Y.-Z.; Wang, H.-H.; Zhang, X.; Zhang, J.-J.; Chen, Z.-N. *Dalton Trans.* **2013**, *42*, 13092−13100. (d) Kobayashi, A.; Masako, K. *Eur. J. Inorg. Chem.* **2014**, 4469−4483.

(5) (a) Yeh, T.-S.; Chu, C.-S.; Lo, Y.-L. *Sens. Actuators, B* **2006**, *119*, 701−707. (b) Guo, H.; Ji, S.; Wu, W.; Shao, J.; Zhao, J. *Analyst* **2010**, *135*, 2832−2840. (c) Wu, W.; Ji, S.; Wu, W.; Zhao, J.; Guo, H. *Dalton Trans.* **2011**, *40*, 11550−11561.

(6) (a) Mauro, M.; Aliprandi, A.; Septiadi, D.; Kehr, N. S.; De Cola, L. *Chem. Soc. Rev.* **2014**, *43*, 4144−4166. (b) Baggaley, E.; Weistein, J.; Williams, J. A. *Coord. Chem. Rev.* **2012**, *256*, 1762−1785.

(7) (a) Anbalagan, V.; Srivastava, T. S. *J. Photochem. Photobiol., A* **1995**, *89*, 113−119. (b) Nolan, D.; Gil, B.; Wang, L.; Zhao, J.; Draper, S. M. *Chem.—Eur. J.* **2013**, *19*, 15615−15626. (c) Stacey, O. J.; Pope, S. J. A. *RSC Adv.* **2013**, *3*, 25550−25564. (d) Lai, S. W.; Liu, Y.; Zhang, D.; Wang, B.; Lok, C. N.; Che, C. M.; Selke, M. *Photochem. Photobiol.* **2010**, *86*, 1414−1420.

(8) (a) Rosenberg, B.; Van Camp, L.; Trosko, J. E.; Mansour, V. H. *Nature* **1969**, *222*, 385−386. (b) Pages, B. J.; Ang, D. L.; Wright, E. P.; Adrich-Wright, J. R. *Dalton Trans.* **2015**, *44*, 3505−3526. (c) Peyratout, C. S.; Aldridge, T. K.; Crites, D. K.; McMillin, D. R. *Inorg. Chem.* **1995**, *34*, 4484−4489. (d) Wang, A. H.-J.; Nathans, J.; van der Marel, G. A.; van Boom, J. H.; Rich, A. *Nature* **1978**, *276*, 471−474.

(9) Holford, J.; Raynaud, F.; Murrer, B. A.; Grimaldi, K.; Hartley, J. A.; Abrams, M.; Kelland, L. R. *Anti-Cancer Drug Des.* **1998**, *13*, 1−18.

(10) For example, see: Brooks, J.; Babayan, Y.; Lamansky, S.; Djurovich, P. I.; Tsyba, I.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2002**, *41*, 3055−3066.

(11) Botchway, S. W.; Charnley, M.; Haycock, J. W.; Parker, A. W.; Rochester, D. L.; Weinstein, J. A.; Williams, J. A. G. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 16071−16076.

(12) (a) Valensin, D.; Gabbiani, C.; Messori, L. *Coord. Chem. Rev.* **2012**, *256*, 2357−2366. (b) Barnham, K. J.; Kenche, V. B.; Ciccotosto, G. D.; Smith, D. P.; Tew, D. J.; Liu, X.; Perez, K.; Cranston, G. A.; Johanssen, T. J.; Volitakis, I.; Bush, A. I.; Masters, C. L.; White, A. R.; Smith, J. P.; Cherny, R. A.; Cappai, R. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 6813. (c) Collin, F.; Sasaki, I.; Eury, H.; Faller, P.; Hureau, C. *Chem. Commun.* **2013**, *49*, 2130−2132.

(13) Coles, S. J.; Gale, P. A. *Chem. Sci.* **2012**, *3*, 683−689.

(14) *CrystalClear-SM Expert 3.1 b27*; Rigaku, 2013

(15) *CrysAlisPro*, version 1.171.37.31; Agilent Technologies, 2014.

(16) Shedrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3−8.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision E.01; Gaussian, Inc.: Wallingford, CT, 2004.



DOI: 10.1021/acs.inorgchem.5b00817
*Inorg. Chem.* XXXX, XXX, XXX−XXX

(18) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.
(19) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chem. Acc.* **1990**, *77*, 123−141.
(20) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (c) Hariharan, P. C.; Pople, J. A. *Theor. Chem. Acc.* **1973**, *28*, 213−222.
(21) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999−3093.
(22) Monti, L.; Franchi, G. *Gazz. Chim. Ital.* **1951**, *81*, 544−547.
(23) Spencer, M.; Santoro, A.; Freeman, G. R.; Diez, A.; Murray, P. R.; Torroba, J.; Whitwood, A. C.; Yellowlees, L. J.; Williams, J. A. G.; Bruce, D. W. *Dalton Trans.* **2012**, *41*, 14244−14256.
(24) (a) Routledge, J. D.; Hallett, A. J.; Platts, J. A.; Horton, P. N.; Coles, S. J.; Pope, S. J. A. *Eur. J. Inorg. Chem.* **2012**, 4065−4075. (b) Jones, J. E.; Jenkins, R. L.; Hicks, R. S.; Hallett, A. J.; Pope, S. J. A. *Dalton Trans.* **2012**, *41*, 10−373−10381.
(25) Godbert, N.; Pugliese, T.; Aiello, I.; Bellusci, A.; Crispini, A.; Ghedini, M. *Eur. J. Inorg. Chem.* **2007**, 5105−5111.
(26) Black, D. S.; Deacon, G. B.; Edwards, G. L. *Aust. J. Chem.* **1994**, *47*, 217−227.
(27) Santoro, A.; Whitwood, A. C.; Williams, J. A. G.; Kozhevnikov, V. N.; Bruce, D. W. *Chem. Mater.* **2009**, *21*, 3871−3882.
(28) Shavaleev, N. M.; Adams, H.; Best, J.; Edge, R.; Navaratnam, S.; Weinstein, J. A. *Inorg. Chem.* **2006**, *45*, 9410−9415.
(29) Esmaeilbeig, A.; Samouei, H.; Abedanzadeh, S.; Amirghofran, Z. *J. Organomet. Chem.* **2011**, *696*, 3135−3142.
(30) Jenkins, D. M.; Senn, J. F.; Bernhard, S. *Dalton Trans.* **2012**, *41*, 8077−8085.
(31) Smith, R. A.; Stokes, E. C.; Langdon-Jones, E. E.; Platts, J. A.; Kariuki, B. M.; Hallett, A. J.; Pope, S. J. A. *Dalton Trans.* **2013**, *42*, 10347−10357.
(32) Cho, J. Y.; Suponitsky, K. Y.; Li, J.; Tirnofeeva, T. V.; Barlow, S.; Marder, S. R. *J. Organomet. Chem.* **2005**, *690*, 4090−4093.
(33) (a) Yersin, H., Volger, A., Eds. *Photochemistry and Photophysics of Coordination Compounds*; Springer-Verlag: Berlin, 1987. (b) Cameron, R. E.; Bocarsly, A. B. *Inorg. Chem.* **1986**, *25*, 2910−2913.
(34) Ghavale, N.; Wadawale, A.; Dey, S.; Jain, V. K. *J. Organomet. Chem.* **2010**, *695*, 1237−1245.
(35) Still, B. M.; Kumar, P. G. A.; Aldrich-Wright, J. R.; Price, W. S. *Chem. Soc. Rev.* **2007**, *36*, 665−686.
(36) Pazderski, L.; Pawlak, T.; Sitkowski, J.; Kozerski, L.; Szlyk, E. *Magn. Reson. Chem.* **2009**, *47*, 932−941.
(37) Bossi, A.; Rausch, A. F.; Leitl, M. J.; Czerwieniec, R.; Whited, M. T.; Djurovich, P. I.; Yersin, H.; Thompson, M. E. *Inorg. Chem.* **2013**, *52*, 12403−12415.
(38) Alvarez, S. *Dalton Trans.* **2013**, *42*, 8617−8636.
(39) (a) Ghedini, M.; Pugliese, T.; La Deda, M.; Godbert, N.; Aiello, I.; Amati, M.; Belviso, S.; Lelj, F.; Accorsi, G.; Barigelletti, F. *Dalton Trans.* **2008**, 4303−4318. (b) Kourkoulos, D.; Karakus, C.; Hertel, D.; Alle, R.; Schmeding, S.; Hummel, J.; Risch, N.; Holder, E.; Meerholz, K. *Dalton Trans.* **2013**, *42*, 13612−13621.
(40) Hudson, Z. M.; Blight, B. A.; Wang, S. N. *Org. Lett.* **2012**, *14*, 1700−1703.



DOI: 10.1021/acs.inorgchem.5b00817
*Inorg. Chem.* XXXX, XXX, XXX−XXX