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Nickel(II), copper(I) and zinc(II) complexes supported by a (4-diphenylphosphino)phenanthridine ligand

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ABSTRACT

A synthetic route to 4-bromophenanthridine has been devised, enabling the construction of (4-diphenylphosphino)phenanthridine (**1**), a heterobifunctional Lewis base containing both phosphine and phenanthridine donors. The coordination chemistry of **1** with ions of late first-row transition metals nickel, copper and zinc has been explored, leading to the isolation and characterization of an organometallic Ni(II) complex, chloro(1-naphthyl)[(4-diphenylphosphino)phenanthridine]nickel (**2**), a halide-bridged copper(I) complex, bromo[(4-diphenylphosphino)phenanthridine]copper dimer (**3**), and a Zn(II) complex, *bis*(chloro)[(4-diphenylphosphino)phenanthridine]zinc (**4**). The solid-state structures of **2**-**4** demonstrate the ability of **1** to support both square planar and tetrahedral geometries. Electrochemical and luminescence studies revealed both metal and ligand-based redox activity and emissive properties.

KEYWORDS

Phenanthridine, heteroleptic ligands, benzo-fused heterocycles, luminescence, redox-active ligands

1. INTRODUCTION

The potential for strong, directional bonding to metal ions, in conjunction with an electronically accessible extended π-system, has spurred the use of benzo-fused *N*-heterocycle-based ligand frameworks in coordination chemistry and enabled a number of useful applications. For example, metal complexes of 8-hydroxyquinoline have had foundational impact in the development of organometallic light emitting diodes [1], while complexes of 1,10-phenanthrolines [2] have been applied in fields ranging from optoelectronics [3] to the construction of molecular machines [4], small-molecule activation and catalysis [5].

In contrast to better-known relatives quinoline [6] and acridine [7], phenanthridine is less common in ligand frameworks. As a monodentate ligand, phenanthridine can be found in the platin drug candidate *cis*-[Pt(NH_3)$_2$(phenanthridine)Cl]NO_3 (phenanthriplatin), which exhibits novel antineoplastic behaviour compared to its pyridine congener [8]. *Tris*(4-phenanthridinolato) complexes of lithium [9] and aluminum [10] have been utilized as emissive components of electroluminescent devices. Atropisomeric phosphinamine ligands (*R*) and (*S*)-6-(2'- diphenylphosphino-l'-naphthyl) phenanthridines were explored for use in Pd-catalyzed allylic alkylation reactions [11]. Re(I) complexes of *fac*-binding, tridentate bis(phenanthridinylmethyl)amines show suitable luminescence properties (red-shifted absorption maxima, lower excitation energies, large Stokes shifts, reduced sensitivity towards dioxygen quenching and emission in the orange range of the visible spectrum) for live-cell fluorescence imaging applications [12]. In comparison, there has been a recent resurgence of interest in the organic chemistry, biological activity, and photophysical properties of phenanthridine itself [13].

In this work, we report the construction of (4-diphenylphosphino)phenanthridine, a heterobifunctional hard/soft Lewis base containing both phosphine and phenanthridine donor units, and its coordination chemistry towards transition metal ions. Metal complexes of (4-diphenylphosphino)phenanthridine show redox activity and luminescence attributable to the presence of a phenanthridinyl unit in the ligand backbone.

2. MATERIALS AND METHODS

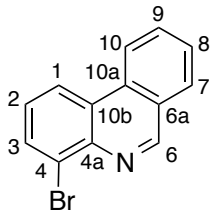
2.1 General Considerations

All air-sensitive manipulations were carried out either in a N_2-filled glove box or by using standard Schlenk techniques under Ar atmosphere. 2,6-dibromoaniline (AK Scientific), 2-formylphenyl boronic acid (Combi Blocks), Pd(PPh_3)$_4$ (Alfa Aesar), Na_2CO_3 (Alfa Aesar), chlorodiphenylphosphine (VWR), chloro(1-naphthyl)*bis*(triphenylphosphine)nickel(II) (Sigma Aldrich), $ZnCl_2$ (Alfa Aesar) and CuBr (Aldrich) were purchased and used without special purification. Solvents were dried and distilled by using appropriate drying agents and were oxygen free prior to use. 1,2-Dimethoxyethane was deoxygenated by three freeze-pump-thaw cycles prior to use in cross-coupling reactions but otherwise used as received. NMR spectra were recorded on a Bruker Avance 300 MHz or Bruker Avance-III 500 MHz spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to residual solvent peaks [14] and assigned with the help of 2D ^{1}H-^{1}H COSY and ^{1}H-^{13}C HSQC/HMBC NMR spectra. Electronic absorption spectra (750–190 nm) were recorded on a Thermo Scientific Genesys 10S UV–Vis spectrophotometer at room temperature. Steady-state fluorescence spectra were collected using a Fluorolog-3 Horiba Jobin Yvon spectrofluorometer (Edison, NJ). Fluorescence spectra were collected using wavelengths set to 380 nm ($\lambda_{excitation}$ for emission spectrum) and 440 nm ($\lambda_{observed}$ for excitation spectrum) for **3** and 360 nm ($\lambda_{excitation}$ for emission spectrum) and 400 nm ($\lambda_{observed}$ for excitation spectrum) for **4**; excitation and emission slits were set to 5 nm (**3**) and 2 nm (**4**) band pass resolution. All samples were measured at room temperature (22 °C) and held in 10 × 10 mm^2 quartz cuvettes. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, BC (Canada). Cyclic

voltammetry was carried out using a CH Instruments 400C Series electrochemical analyzer/workstation in conjunction with a three-electrode cell. A BASi glassy carbon disk electrode (3.0 mm diameter) was used as the working electrode, a platinum wire the counter electrode, with a non-aqueous Ag/Ag^+ quasi-reference electrode separated from the solution by a porous Teflon tip. All cyclic voltammetry (CV) measurements were conducted in CH_2Cl_2 with 0.1 M nBu$_4$NPF$_6$ as the supporting electrolyte, at scan rates ranging from 50 mV/s to 800 mV/s. Ferrocene was added to each solution as an internal reference, allowing the potentials to be referenced to the $Fe(\eta^5\text{-}C_5H_5)_2/Fe(\eta^5\text{-}C_5H_5)_2^+$ redox couple.

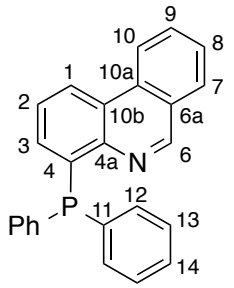
2.2 Synthesis of compounds

*2.2.1 Preparation of 4-bromophenanthridine (**1-Br**)*



Representative run: 2,6-dibromoaniline (1.01 g, 4.02 mmol) and $Pd(PPh_3)_4$ (0.09 g, 0.08 mmol) were added to a flask fitted with a condenser and charged with 1,2-dimethoxyethane (15 mL) under an Ar atmosphere. After ~15 min of stirring, 2-formylphenylboronic acid (0.66 g, 4.4 mmol) was added and stirring was continued for another 15 min. A deoxygenated solution of sodium carbonate (1.06 g, 0.01 mol) in 8 mL of distilled water was added. The reaction mixture was refluxed at 100 °C for 5 h with stirring. Then reaction mixture was cooled to room temperature and the volatiles were removed under reduced pressure. The remaining residue was extracted using dichloromethane (80 mL) and the extract was filtered and dried. 4-Bromophenanthridine was isolated as a light yellow solid following column chromatography on activated neutral alumina using toluene as eluent (R_f = 0.21). Yield = 0.35 g (35 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 9.39 (s, 1H, C_6-*H*), 8.59 (d - overlapped, J_{HH} = 8.4 Hz, 1H, C_{10}/C_1-*H*), 8.55 (d – overlapped, J_{HH} = 8.4 Hz, 1H, C_{10}/C_1-*H*), 8.08 (overlapped d, J_{HH} = 7.8 Hz, 2H, C_3/C_7-*H*), 7.89 (app t, J= 7.5 Hz, 1H, C_9-*H*), 7.75 (app t, J= 7.5 Hz, 1H, C_8-*H*), 7.52 ppm (dt, J_{HH} = 7.8, 1.2 Hz, 1H, C_2-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 25 °C): δ 154.5 (C_6=N), 141.8 (C_{4a}), 132.7 (C_3), 132.5 (C_{10a}), 131.7 (C_9), 129.2 (C_7), 128.3 (C_8), 127.6 (C_2), 126.6 (C_{6a}), 126.1 (C_4-Br), 125.9 (C_{10b}), 122.2 (C_1), 122.1 ppm (C_{10}).

*2.2.2 Preparation of (4-diphenylphosphino)phenanthridine (**1**)*



A solution of *sec*-butyllithium (1.6 M, 3.2 mL, 4.0 mmol) in cyclohexane was added dropwise to a stirring solution of 4-bromophenanthridine (1.03 g, 4.00 mmol) in Et_2O (5 mL) at -78 °C over a period of 15 min. Stirring was then continued for additional 4 h while maintaining the same temperature. A solution of chlorodiphenylphosphine (0.88 g, 4 mmol) in Et_2O (2 mL) was added drop-wise and the reaction mixture was allowed to warm to room temperature. A white precipitate formed. The volatiles were removed under reduced pressure and the remnant dissolved in dichloromethane (40 mL) and filtered through a small plug of Celite. The filtrate was dried under vacuum to give a light yellow solid, which was then washed with degassed ethanol (50 mL). Yield = 1.05 g (72%). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 9.23 (s, 1H, C_6-*H*), 8.64 (d - overlapped, J_{HH} = 8.4 Hz, 1H, C_{10}-*H*), 8.59 (d - overlapped, J_{HH} = 8.4 Hz, 1H, C_1-*H*), 8.02 (d, J_{HH} = 7.8 Hz, 1H, C_7-*H*), 7.87 (app t, *J* = 8 Hz, 1H), 7.71 (app t, *J* = 8 Hz, 1H), 7.57 (app t, *J* = 8 Hz, 1H), 7.33-7.30 (m, 10H), 7.37-7.28 (br, 10H), 7.13 ppm (dd, *J* = 7.2, 3.6 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 25 °C): δ 152.8 (*C*$_6$=N), 146.1 (d, J_{CP} = 17 Hz, C_{4a}), 139.1 (d, J_{CP} = 11 Hz, P-C_4), 138.0 (d, J_{CP} = 44 Hz, P-C_{11}), 134.3 (d, J_{CP} = 20 Hz, PC_{12}), 133.4 (*C*$_3$-H), 132.7 (C_{10a}), 131.1 (*C*$_9$-H), 129.0 (*C*$_7$-H), 128.5 (d, J_{CP} = 5 Hz, P-C_{13}), 128.4 (P-C_{14}), 127.7(*C*$_8$-H), 127.1 (*C*$_2$-H), 126.5 (C_{6a}), 123.8 (d, J_{CP} = 2 Hz, C_{10b}) 123.2 (*C*$_1$-H), 122.2 ppm (C_{10}-H). ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz, 25 °C): δ -13.7 (s) ppm. Anal. Calc'd for $C_{25}H_{18}N_1P_1$: C, 82.63; H, 4.99. Found: C, 82.87; H, 5.39.

Single crystals of **1** suitable for X-ray diffraction were grown via diffusion of hexanes vapors into a CH_2Cl_2 solution. Crystal structure data for **1**: $C_{25}H_{18}NP$, 363.37 g/mol, monoclinic, space group $P2_1/c$; a = 12.800(3) Å, b = 9.4949(19) Å, c = 15.887(3) Å, β = 100.74(3)°, V = 1897.0(7) Å^3; Z = 4, ρ_{calcd} = 1.272 g cm^{-3}; crystal dimensions: 0.20 × 0.20 × 0.15 mm; diffractometer: Bruker APEXII CCD; Mo Kα radiation, ω scans, 293(2) K, 2.511 ≤ θ ≤ 30.059°; 21514 reflections, 5550 independent (R_{int} = 0.0150), direct methods; absorption coeff (μ = 0.154 mm^{-1}), absorption correction: semi-empirical from equivalents; completeness to θ = 25.242°: 99.9%; refinement (against F^2) with SHELXL-2014/7, 244 parameters, 0 restraints, R_1 = 0.0439 ($I > 2\sigma$) and wR_2 = 0.1641 (all data), Goof = 1.357, residual electron density 0.267/−0.330 e Å^{-3}.

*2.2.3 Preparation of {(4-diphenylphosphino)phenanthridine}Ni(1-naphthyl)Cl (**2**).*

A solution of (4-diphenylphosphino)phenanthridine (0.045 g, 0.125 mmol) in CH_2Cl_2 (2.5 mL) was added slowly to a solution of chloro(1-naphthyl)*bis*(triphenylphosphine)nickel(II) (0.093 g, 0.125 mmol) in CH_2Cl_2 (2.5 mL) to give an orange solution. The reaction mixture was stirred for 4 h, after which the volatiles were removed under reduced pressure. The

solid residue was washed with diethyl ether (3 x 10 mL) and dried under vacuum to give a red-orange solid. Yield = 0.067 g (92%). ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 10.61 (s, 1H, $^{phen}C_{Ar}$-*H*), 9.13 (d, *J* = 8.3 Hz, 1H, $^{phen}C_{Ar}$-*H*), 8.70 (d, *J* = 7.7 Hz, 1H, $^{phen}C_{Ar}$-*H*), 8.60 (d, *J* = 8.3 Hz, 1H, $^{phen}C_{Ar}$-*H*), 8.28 (d, *J* = 7.9 Hz, 1H), 8.20 (d, *J* = 7.5 Hz, 1H, $^{phen}C_{Ar}$-*H* or PC_{Ar}-*H*), 8.17 (d, *J* = 7.5 Hz, 1H, $^{phen}C_{Ar}$-*H* or PC_{Ar}-*H*), 8.01 (app t, *J* = 7.7 Hz, 1H), 7.82 (app t, *J* = 7.5 Hz, 1H), 7.72 (dt, *J* = 18.7, 7.3 Hz, 2H, PC_{Ar}-*H*), 7.48 (dt, *J* = 7.4, 4.2 Hz, 1H, PC_{Ar}-*H*), 7.44 (td, *J* = 7.4, 7.0, 2.1 Hz, 2H, PC_{Ar}-*H*), 7.36 (d, *J* = 8.1 Hz, 1H, PC_{Ar}-*H*), 7.30 (d, *J* = 7.0 Hz, 1H, PC_{Ar}-*H*), 7.15 (d, *J* = 8.0 Hz, 1H, PC_{Ar}-*H*), 7.04 (overlapping m, 2H, C_{napth}-*H* and PC_{Ar}-*H*), 6.87 (overlapping dd, *J* = 7.5, 2.5 Hz, 2H, C_{napth}-*H*), 6.78 (overlapping dd, *J* = 8.0, 2.5 Hz, 2H, C_{napth}-*H*), 6.52 (d, *J* = 7.5 Hz, 1H, C_{napth}-*H*), 6.49 ppm (d, *J* = 7.5 Hz, 1H, C_{napth}-*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz, 25 °C): δ 159.2 ($^{phen}C_{Ar}$-H), 147.7 (d, J_{CP} = 21 Hz, $^{phen}C_{Ar}$), 143.2 (d, J_{CP} = 48 Hz, C_{napth}), 140.2 (C_{napth}), 135.5 (d, J_{CP} = 4 Hz, PC_{Ar}-H), 134.0 (d, J_{CP} = 2 Hz, $^{phen}C_{Ar}$), 133.8 (PC_{Ar}-H), 133.7 ($^{phen}C_{Ar}$-H), 133.6 ($^{phen}C_{Ar}$-H), 133.4 (d, J_{CP} = 2 Hz, PC_{Ar}-H), 133.5 (d, J_{CP} = 34 Hz, $^{phen}C_{Ar}$), 132.9 ($^{phen}C_{Ar}$ -H), 132.5 (C_{napth}-H), 132.4 (C_{napth}-H), 132.2 ($^{phen}C_{Ar}$), 131.3 (d, J_{CP} = 2 Hz, PC_{Ar}-H), 130.9 ($^{phen}C_{Ar}$-*H*), 130.6 (d, J_{CP} = 56 Hz, PC_{Ar}), 130.0 (d, J_{CP} = 2 Hz, PC_{Ar}-H), 129.2 ($^{phen}C_{Ar}$-H), 129.0 (d, J_{CP} = 11 Hz, PC_{Ar}-H), 128.3 (d, J_{CP} = 6 Hz, C-H, PC_{Ar}-H), 127.8 (C_{napth}-H), 127.7 (C_{napth}-H), 127.5 (PC_{Ar}-H), 126.8 ($^{phen}C_{Ar}$), 126.6 (d, J_{CP} = 60 Hz, PC_{Ar}-H), 126.0 ($^{phen}C_{Ar}$-H), 125.9 ($^{phen}C_{Ar}$), 123.9 (C_{napth}-H), 123.8 (C_{napth}-H), 123.2 (C_{napth}-H), 122.6 (C_{napth}), 122.1 ppm ($^{phen}C_{Ar}$-*H*). ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz, 25 °C): δ 30.6 ppm (s). UV-Vis: λ (ε) 298 (2.17 x 10^4), 306 (2.03 x 10^4), 325 (1.39 x 10^4), 335 (1.18 x 10^4), 358 (6.60 x 10^3), 397 nm (5.44 x 10^3 $M^{-1}cm^{-1}$). Anal. Calc'd for $C_{35}H_{25}N_1P_1Ni_1$: C, 71.90; H, 4.31. Found: C, 71.16; H, 4.67.

Single crystals of sufficient quality for X-ray diffraction were grown from dichloromethane/hexane at -35 °C. Crystal structure data for **2**: $C_{37}H_{29}Cl_5NNiP$, 754.54 g/mol, monoclinic, space group $P2_1/c$; a = 10.135(2) Å, b = 13.559(3) Å, c = 25.353(5) Å, β = 91.65(3)°, V = 3482.7(12) $Å^3$; Z = 4, ρ_{calcd} = 1.439 g cm^{-3}; crystal dimensions: 0.14 × 0.10 × 0.06 mm; diffractometer: Bruker APEXII CCD; Mo Kα radiation, ω scans, 298(2) K, 2.200 ≤ θ ≤ 27.477°; 20539 reflections, 7980 independent (R_{int} = 0.0296), direct methods; absorption coeff (μ = 1.015 mm^{-1}), absorption correction: semi-empirical from equivalents; completeness to θ = 26°: 99.9%; refinement (against F^2) with SHELXL-2014/7, 406 parameters, 0 restraints, R_1 = 0.0480 ($I > 2\sigma$) and wR_2 = 0.1458 (all data), Goof = 1.010, residual electron density 0.633/−0.834 e $Å^{-3}$.

*2.2.4 Preparation of {(4-diphenylphosphino)phenanthridine}CuBr (**3**).*

A solution of (4-diphenylphosphino)phenanthridine (0.023 g, 0.063 mmol) in CH_2Cl_2 (3 mL) was added drop-wise to a suspension of CuBr (0.089 g, 0.063 mmol) in CH_2Cl_2 (3 mL) with constant stirring. The reaction mixture was stirred for overnight at room temperature. Then the reaction mixture was filtered through small plug of Celite and dried under vacuum to give an orange solid. Yield = 0.022 g (71 %). ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 9.66 (s, 1H, $^{phen}C_{Ar}$-*H*), 8.73 (dd, *J* = 8.1, 1.3 Hz, 1H, $^{phen}C_{Ar}$-*H*), 8.63 (d, *J* = 8.3 Hz, 1H, $^{phen}C_{Ar}$-*H*), 7.93 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1H, $^{phen}C_{Ar}$-*H*), 7.86 – 7.80 (m, 2H, $^{phen}C_{Ar}$-*H*), 7.76 (t, *J* = 7.6 Hz, 1H, $^{phen}C_{Ar}$-*H*), 7.69 (t, *J* = 7.5 Hz, 1H, $^{phen}C_{Ar}$-*H*), 7.63 –

7.56 (m, 4H, PC_{Ar}-*H*), 7.38 (td, *J* = 7.4, 1.6 Hz, 2H, PC_{Ar}-*H*), 7.33 ppm (ddd, *J* = 8.8, 6.5, 1.9 Hz, 4H, PC_{Ar}-*H*). ^{13}C NMR ($CDCl_3$, 500 MHz, 25 °C): δ 155.8 (d, J_{CP} = 4 Hz, $^{phen}C_{Ar}H$), 145.2 (d, J_{CP} = 16 Hz, $^{phen}C_{Ar}$), 135.6 ($^{phen}C_{Ar}H$), 135.0 (d, J_{CP} = 33 Hz, $^{phen}C_{Ar}$), 133.9 (d, J_{CP} = 16 Hz, P$C_{Ar}H$), 132.8 ($^{phen}C_{Ar}$), 132.7 ($^{phen}C_{Ar}H$), 132.4 (d, J_{CP} = 28 Hz, PC_{Ar}), 130.1 (P$C_{Ar}H$), 130.0 ($^{phen}C_{Ar}H$), 129.0 (d, J_{CP} = 10 Hz, $PC_{Ar}H$), 128.7 ($^{phen}C_{Ar}H$), 127.7 (d, J_{CP} = 5 Hz, $^{phen}C_{Ar}H$), 126.8 (d, J_{CP} = 3 Hz, $^{phen}C_{Ar}$), 125.4 (d, J_{CP} = 4 Hz, $^{phen}C_{Ar}H$), 125.3 (br, $^{phen}C_{Ar}$), 122.2 ppm ($^{phen}C_{Ar}H$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz, 25 °C): δ -24 ppm (br s). UV-Vis: λ (ε) 278 (2.30 x 10^4), 299 (1.67 x 10^4), 312 (sh, 1.33 x 10^4), 335 (5.23 x 10^3), 353 nm (4.28 x 10^3 $M^{-1}cm^{-1}$). Anal. Calc'd for $C_{50}H_{36}N_2P_2Cu_2Br_2 \bullet CH_2Cl_2$: C, 55.76; H, 3.49. Found: C, 55.84; H, 3.27. One molecule of CH_2Cl_2 (the crystallization solvent) per dimer was present in the crystal lattice, and was observed by ^{1}H NMR spectroscopy upon dissolution of crystals of **3**.

X-ray quality crystals were grown in CH_2Cl_2/diethylether at room temperature. Crystal structure data for **3**: $C_{51}H_{38}Br_2Cl_2Cu_2N_2P_2$, 1098.57 g/mol, triclinic, space group $P\bar{1}$; a = 10.895(2) Å, b = 13.323(3) Å, c = 16.828(3) Å, α = 99.27(3)°, β = 98.23(3)°, γ = 99.89(3)°, V = 2337.9(9) $Å^3$; Z = 2, ρ_{calcd} = 1.561 g cm^{-3}; crystal dimensions: 0.580 × 0.025 × 0.15 mm; diffractometer: Bruker APEXII CCD; Mo Kα radiation, ω scans, 293(2) K, 2.103 ≤ θ ≤ 27.597°; 21522 reflections, 10796 independent (R_{int} = 0.0233), direct methods; absorption coeff (μ = 2.839 mm^{-1}), absorption correction: semi-empirical from equivalents; completeness to θ = 26°: 99.9%; refinement (against F^2) with SHELXL-2014/7, 550 parameters, 0 restraints, R_1 = 0.0424 ($I > 2\sigma$) and wR_2 = 0.1299 (all data), Goof = 1.001, residual electron density 1.016/−0.975 e $Å^{-3}$.

*2.2.5 Preparation of {(4-diphenylphosphino)phenanthridine}$ZnCl_2$ (**4**).*

A solution of (4-diphenylphosphino)phenanthridine (0.023 g, 0.063 mmol) in THF (2.5 mL) was added dropwise to a solution of $ZnCl_2$ (0.0085 g, 0.063 mmol) in THF (2.5 mL) with constant stirring. The mixture was stirred for additional 3 h, at which point the formation of a white suspension was noted. The reaction mixture was dried under reduced pressure and dissolved in the dichloromethane (5 mL) and filtered over Celite. Concentration and recrystallization from dichloromethane/hexane at room temperature gave colorless crystals. Yield = 0.026 g (83 %). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 9.57 (s, 1H, N=C-*H*), 8.89-8.77 (m, 1H, $^{phen}C_{Ar}$-*H*), 8.67 (d, J_{HH} = 8.4 Hz, 1H, $^{phen}C_{Ar}$-*H*), 8.18 (dd, J_{HH} = 8.1, 1.2 Hz, 1H, $^{phen}C_{Ar}$-*H*), 8.05 (ddd, J = 8.4, 7.1, 1.3 Hz, 1H, $^{phen}C_{Ar}$-*H*), 7.95-7.81 (overlapped m, 3H, $^{phen}C_{Ar}$-*H*), 7.69 (overlapped m, 4H, PC_{Ar}-*H*), 7.52-7.43 ppm (overlapped m, 6H, PC_{Ar}-*H*). ^{13}C NMR ($CDCl_3$, 126 MHz, 25 °C): δ 156.7 (d, J_{CP} = 4 Hz, $^{phen}C_{Ar}H$), 142.8 (d, J_{CP} = 14 Hz, $^{phen}C_{Ar}$), 136.4 ($^{phen}C_{Ar}H$), 134.5 ($^{phen}C_{Ar}H$), 134.2 (d, J_{CP} = 14 Hz, P$C_{Ar}H$), 133.4 (d, J_{CP} = 2 Hz, $^{phen}C_{Ar}$),131.8 (d, J_{CP} = 2 Hz, $^{phen}C_{Ar}H$), 130.8 ($^{phen}C_{Ar}H$), 129.7 (P$C_{Ar}H$), 129.6 (P$C_{Ar}H$), 128.9 (d, J_{CP} = 34 Hz, $^{phen}C_{Ar}$), 128.6 (d, J_{CP} = 6 Hz, $^{phen}C_{Ar}H$), 126.9 (d, J_{CP} = 1 Hz, $^{phen}C_{Ar}H$), 126.3 (d, J_{CP} = 3 Hz, $^{phen}C_{Ar}$), 126.2 (d, J_{CP} = 39 Hz, PC_{Ar}), 125.9 (d, J_{CP} = 4 Hz, $^{phen}C_{Ar}$), 122.4 ($^{phen}C_{Ar}H$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz, 25 °C): δ -32.4 (s) ppm. UV-Vis: λ (ε) 238 (2.60 x 10^4), 253 (2.89 x 10^4), 301 (5.68 x 10^3), 341 (2.49 x 10^3), 357 nm (2.13 x 10^3 $M^{-1}cm^{-1}$). Anal. Calc'd for $C_{25}H_{18}N_1P_1Zn_1Cl_2 \bullet 0.5(CH_2Cl_2)$: C, 56.49; H, 3.53. Found: C, 56.69; H, 3.67. Half a molecule of CH_2Cl_2 (the crystallization solvent) was found in the asymmetric unit of the

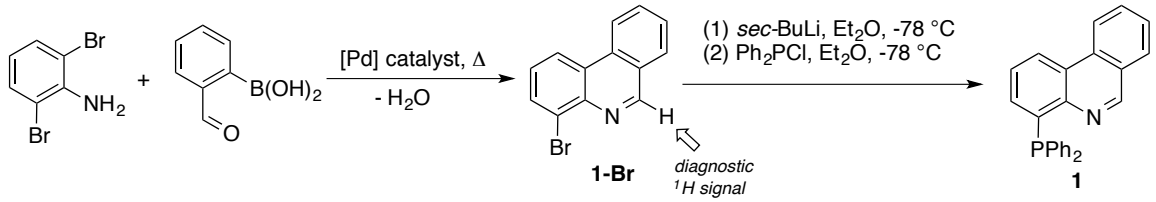
X-ray structure of **4**, and could also be seen by ^{1}H NMR spectroscopy upon dissolution of crystals of **4**.

Crystal structure data for **4**: $C_{51}H_{38}Cl_6N_2P_2Zn_2$, 1084.21 g/mol, monoclinic, space group *C*2/c; a = 17.297(4) Å, b = 8.0754(16) Å, c = 34.424(7) Å, β = 94.02(3)°, V = 4796.4(17) Å^3; Z = 4, ρ_{calcd} = 1.501 g cm^{-3}; crystal dimensions: 0.125 × 0.055 × 0.025 mm; diffractometer: Bruker APEXII CCD; Mo Kα radiation, ω scans, 293(2) K, 2.361 ≤ θ ≤ 27.511°; 21325 reflections, 5540 independent (R_{int} = 0.0237), direct methods; absorption coeff (μ = 1.439 mm^{-1}), absorption correction: semi-empirical from equivalents; completeness to θ = 26°: 100%; refinement (against F^2) with SHELXL-2014/7, 285 parameters, 0 restraints, R_1 = 0.0392 ($I > 2\sigma$) and wR_2 = 0.1181 (all data), Goof = 1.037, residual electron density 0.976/−0.665 e Å^{-3}.

3. RESULTS AND DISCUSSION

3.1 Ligand Synthesis

To access proligand **1**, a preparatory route to 4-bromophenanthridine (**1-Br**) via sequential Pd-catalyzed cross-coupling and condensation was first explored (Scheme 1) [15]. Ray and coworkers recently reported a similar strategy for the production of 2-substituted phenanthridines from *N*-(2-iodo-aryl)-formamides [16]. After screening a range of conditions (Table 1), the most straightforward route using 2,6-dibromoaniline was found to give acceptable conversion to **1-Br**. The target compound shows good solubility in common organic solvents and could be reproducibly isolated as a light yellow solid following column chromatography in low yields (~ 35 %). No significant increase in yield was observed using either 2,6-dibromo-*N*-acetanilide [17] or the trifluoroborate salt of 2-formylboronic acid (entries 7-12). Limiting the amount of water added to the reaction (entries 14-15) shut down reactivity all together.



Scheme 1. Combined Suzuki coupling/condensation route to 4-bromophenanthridine **1-Br** and conversion to **1**.

Table 1. Conditions attempted for the synthesis of **1-Br**.

Entry	Catalyst (mol %)	Base	Solvent	T (°C)	t (h)	Yield[a] (%)
1	$Pd(PPh_3)_4$ (10)	$K_3PO_{4(aq)}$	DMF	100	5	13
2	$Pd(PPh_3)_4$ (10)	$K_3PO_{4(aq)}$	DMF	100	24	13
3	$Pd(PPh_3)_4$ (10)	$K_3PO_{4(aq)}$	Toluene	100	5	9
4	$Pd(PPh_3)_4$ (10)	Na_2CO_3	Toluene/EtOH	100	5	trace

5	$Pd(PPh_3)_4$ (10)	$Na_2CO_{3(aq)}$	DME	100	5	31
6	$Pd(PPh_3)_4$ (2)	$Na_2CO_{3(aq)}$	DME	100	5	32
7[b]	$Pd(PPh_3)_4$ (5)	$Na_2CO_{3(aq)}$	DME	100	5	35
8[b]	$Pd(PPh_3)_4$ (2)	$Na_2CO_{3(aq)}$	DME	100	5	22
10[c]	$Pd(PPh_3)_4$ (10)	$K_3PO_{4(aq)}$	DME	100	5	13
11[c]	$Pd(PPh_3)_4$ (10)	$Na_2CO_{3(aq)}$	DME	100	5	25
12[c]	$Pd(PPh_3)_4$ (5)	$NaHCO_{3(aq)}$	DME	100	5	31
13	$Pd(OAc)_2$ /PPh_3 (0.08:1)	$Na_2CO_{3(aq)}$	DME	100	5	24
14	$Pd(PPh_3)_4$ (2)	Na_2CO_3(anhydrous)	DME	100	5	trace
15[c]	$Pd(PPh_3)_4$ (2)	Na_2CO_3(anhydrous)	DME	100	5	7

[a] Isolated yield following column chromatography.
[b] Potassium trifluoroborate salt of 2-formylphenylboronic acid
[c] 2,6-dibromo-*N*-acetanilide was used in place of 2,6-dibromoaniline

Compound **1-Br** was fully characterized by 1- and 2D ^{1}H and ^{13}C NMR spectroscopy, which confirmed assembly of the asymmetric, bromo-substituted phenanthridine ring system. The ^{1}H NMR spectrum of **1-Br** in $CDCl_3$ revealed a diagnostic downfield singlet for the H in the 6-position at δ_H = 9.39 ppm, with strong one-bond coupling to a corresponding ^{13}C signal at 154.5 ppm (^{13}C-^{1}H HSQC). Using identical reaction conditions in the absence of palladium, the condensation product was not observed. This could mean that carbon-carbon bond formation precedes construction of the C=N bond or that intermolecular condensation is reversible under the reaction and/or isolation conditions investigated.

The diphenylphosphine unit was then installed via lithium-halogen exchange with *sec*-BuLi in diethyl ether at low temperature (-78 °C), followed by quenching with one equivalent of Ph_2PCl at the same temperature. Phosphine **1** was isolated cleanly in 72 % yield as an off-white solid following recrystallization from ethanol (δ□ = -13.7 ppm). An X-ray diffraction study of a single-crystal of **1** (**Fig. 1**) confirmed the structure assigned in solution. The solid-state structure shows a short C(1)=N(1) bond length [1.3005(15) Å] in the central pyridine unit, statistically indistinguishable from the analogous C=N bond in phenanthridine [18] [1.296(3) Å], but shorter than that of 8-(diphenylphosphino)quinoline [1.3196 (17)] [19] and thus may be considered the effect of the third fused ring of the phenanthridine moiety. The bond distances and angles are otherwise unremarkable.

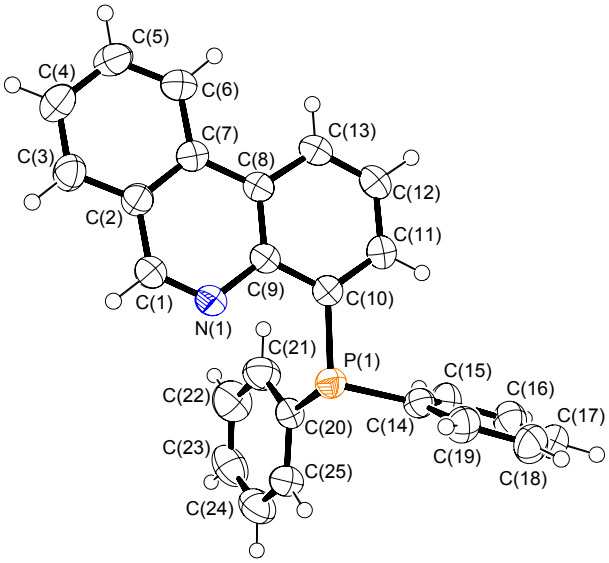


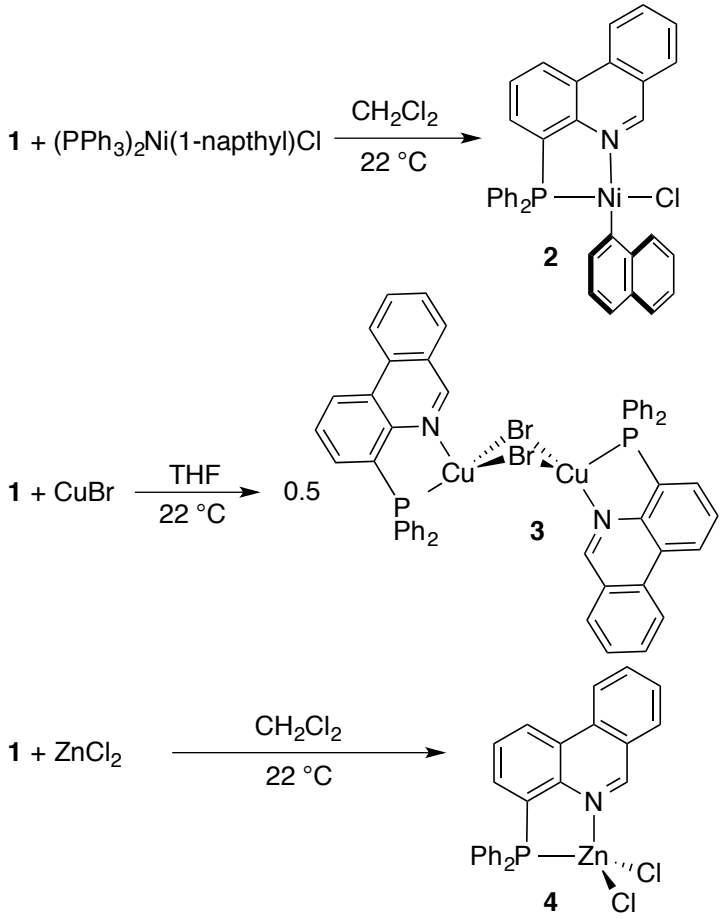
Figure 1. ORTEP [20] of **1** with thermal ellipsoids shown at 50 % probability levels. Selected bond distances (Å) and angles (°): C(1)-N(1) 1.3005(15), C(1)-C(2) 1.4329(16), C(2)-C(7) 1.4085(16), C(7)-C(8) 1.4464(16), C(8)-C(9) 1.4157(14), C(9)-N(1) 1.3865(13), C(10)-P(1) 1.8347(12); C(20)-P(1)-C(10) 102.85(5), C(20)-P(1)-C(14) 100.71(5), C(10)-P(1)-C(14) 102.73(5).

*3.2 Synthesis of Nickel, Copper and Zinc Complexes of **1***

To establish the coordinating ability of **1** towards late transition metals, a series of representative first row metal complexes of Ni, Cu and Zn were targeted (Scheme 2). This series was chosen to allow characterization of complexes of **1** with either redox-active (Ni, Cu) or redox-inactive metals (Zn), as well candidates with potentially interesting photophysical properties (Cu, Zn). The chelating bifunctional ligand **1** readily displaces less strongly bound monodentate ligands such as PPh_3 from chloro(1-naphthyl)*bis*(triphenylphosphine)nickel [21] at room temperature in CH_2Cl_2, evident by the disappearance of the resonance of **1** and the appearance of a new singlet in the $^{31}P\{^1H\}$ NMR spectrum (δ = 30.6 ppm), consistent with formation of a single isomer with the strongly σ-donating napthyl group likely *trans* to the phenanthridinyl unit. From this solution, complex **2** could be isolated in high yield (92 %) as a crystalline red-orange solid. Inequivalent, sharp resonances for each phenyl ring in the -PPh_2 unit are visible in the ^1H NMR spectrum suggesting an orthogonal orientation of the napthyl and phenanthridinyl ring systems and limited rotation about the Ni-carbon bond across a range of temperatures (323-223 K; see Supporting Information, Figure S2). The signal for the diagnostic phenanthridine proton in the 6-position shifts drastically upon coordination to nickel (δ = 10.62 ppm), a shift of 1.5 ppm downfield compared with **1**.

Addition of **1** to a suspension of CuBr in CH_2Cl_2 at room temperature led to dissolution of the metal salt and formation of a deep orange solution. The $^{31}P\{^1H\}$ NMR spectrum of this solution shows a broad peak centered at -24 ppm, in line with ^{31}P chemical shifts reported for 8-(diphenylphosphino)quinoline complexes of Cu(I) [22]. The broad signal is consistent with complexation, the large quadrupolar moment of Cu(I), and the low

symmetry of the complex [23]. An orange, crystalline solid (**3**) was isolated from this solution in good yield (71%). The ^{1}H NMR spectra of the orange crystals showed much sharper features, with the diagnostic phenanthridine again shifted downfield from free **1** (δ = 9.66 ppm). While this signal is slightly broader than that observed for **2** (**3**: FWHM = 24 Hz; **2**: FWHM = 5 Hz), the broadening may be due to coordination to Cu(I) rather than fluxional behaviour as the remaining phenanthridine signals are sharp and well-resolved. Variable temperature ^{1}H NMR spectra collected for **3** (see Supporting Information, Figure S3) revealed a broadening, and sharpening of this diagnostic signal as the temperature is lowered, and a substantial shift from 9.66 ppm (298 K) to 9.89 ppm (223 K). Mixing a THF solution of **1** with a THF solution of $ZnCl_2$ led to the formation of a white precipitate after 3 h of stirring under ambient conditions. Isolation and recrystallization from CH_2Cl_2/hexanes gave colorless crystals of **4** in good yield (83%). Similar to complexes **2** and **3**, the ^{1}H NMR of the Zn complex showed a downfield shift of the diagnostic phenanthridine proton (δ_H = 9.57 ppm).



Scheme 2. Synthesis of metal complexes **2**-**4**.

*3.3 Solid-State Structures of **2-4***

To examine the coordination geometry of **1** with Ni(II), Cu(I) and Zn(II) in the solid state, single-crystal X-ray diffraction studies were undertaken (Figure 2). Orange, X-ray

quality crystals of **2** were grown by diffusion of hexane vapors into a dichloromethane solution at -35 °C. The nickel center is four-coordinate, in a distorted square planar environment, chelated by one equivalent of **1** with retention of both the chloride and 1-napthyl ligands (Figure 2a). As a κ^2-bidentate ligand, **1** forms a five-membered ring upon coordination to Ni, with a slightly acute N(1)-Ni(1)-P(1) angle [87.49(6)°]. The planarity of the 1-napthyl substituent and the phenyl rings on phosphorus means the structure can accommodate a more acute P(1)-Ni(1)-$C(26)_{napthyl}$ angle [86.08(8)°], resulting in a wider N(1)-Ni(1)-Cl(1) angle [95.88(7)°]. The stronger σ-donor (1-naphthyl) is *trans* to the phenanthridinyl donor, consistent with the weaker *trans* influence of the N-donor compared with the PPh_2 arm of **1**. The Ni(1)-C(26) distance in **2** is 1.900(3) Å, not significantly different from the analogous bond distance [1.903(5) Å] in chloro(1-naphthyl)[8-(diphenylphosphino)quinoline]nickel] [24] implying the quinoline and phenathridine donor units of in the two complexes have comparable *trans* influences.

Orange blocks of the copper complex **3** deposited from a dichloromethane/diethylether solution left overnight at room temperature. X-Ray diffraction revealed a dimeric structure in the solid-state, with two [(Ph_2PNPhen)CuBr] units stabilized by a butterfly-shaped [Cu_2Br_2] core (Figure 2b). While solution NMR spectra of **3** showed only one set of ligand resonances for both phenanthridinyl and diphenylphosphino units, the solid-state structure contains crystallographically distinct ligand environments. Each copper atom is in a distorted tetrahedral environment, resulting from the geometric constraints of the chelating P^N ligand [P(2)-Cu(2)-N(2) 85.01(9)°; P(1)-Cu(1)-N(1) 85.34(9)°]. While planar Cu_2X_2 units are more common [25], a series of complexes showing similar butterfly Cu_2X_2 motifs supported by (diphenylphosphino)pyridine-type P^N ligands were recently reported [25]. In that series, a third equivalent of P^N ligand bridges the two Cu centers. The Cu_2X_2 unit in **3** is supported only by bridging halides, with a dihedral angle between the two Br-Cu-Br planes of 149°. The Cu-Cu distance [2.8396(12) Å] is longer than in a related (8-diphenylphosphino)quinoline)copper iodide dimer [2.631(37) Å] that accordingly has a more highly folded Cu_2I_2 core (dihedral angle: 138°) [26].

Using the same recrystallization conditions yielded colorless crystals suitable for X-ray diffraction of the zinc complex **4** (Figure 2c). A similar tetrahedral distortion is observed in the solid-state structure of **4**, imposed again by acute P(1)-Zn(1)-N(1) angle [82.54(6)°]. The smaller angle must be a consequence of the presence of a second large chloride ligand, as the ionic radii of Cu(I) and Zn(II) are identical [27]. The phenanthridine ring system is twisted slightly out of the P-Zn-N plane, removing mirror plane symmetry and rendering the two chlorides crystallographically inequivalent.

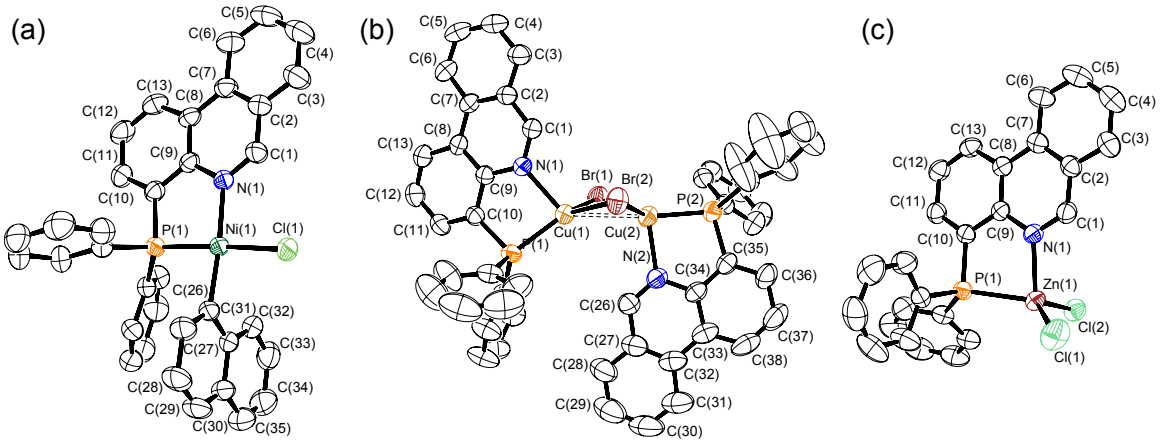


Figure 2. ORTEP [20] of complexes (a) **2**, (b) **3** and (c) **4**, all with thermal ellipsoids shown at 50% probability levels. Hydrogen atoms and labels on phosphine phenyl rings are omitted for clarity. Selected bond distances (Å) and angles (°): **2**: Ni(1)-C(26) 1.900(3), Ni(1)-N(1) 1.996(2), Ni(1)-P(1) 2.1053(9), Ni(1)-Cl(1) 2.2162(9), N(1)-C(1) 1.301(3); N(1)-Ni(1)-P(1) 87.49(6)°, N(1)-Ni(1)-C(26) 95.88(7)°, P(1)-Ni(1)-Cl(1) 86.08(8)°, C(26)-Ni(1)-Cl(1) 90.61(8)°. **3**: Br(1)-Cu(2) 2.4313(11), Br(1)-Cu(1) 2.5119(9), Br(2)-Cu(1) 2.4188(11), Br(2)-Cu(2) 2.4721(9), Cu(1)-N(1) 2.114(3), Cu(1)-P(1) 2.2050(11), Cu(1)···Cu(2) 2.8396(12), Cu(2)-N(2) 2.112(3), Cu(2)-P(2) 2.2049(13), N(1)-C(1) 1.303(4), N(1)-C(9) 1.390(4), N(2)-C(26) 1.303(5), N(2)-C(34) 1.394(5); Cu(2)-Br(1)-Cu(1) 70.10(3), Cu(1)-Br(2)-Cu(2) 70.97(3), N(1)-Cu(1)-P(1) 85.34(9), N(2)-Cu(2)-P(2) 85.01(9). **4**: Zn(1)-N(1) 2.091(2), Zn(1)-Cl(1) 2.1896(10), Zn(1)-Cl(2) 2.2230(8), Zn(1)-P(1) 2.3854(8), N(1)-C(1) 1.305(3), N(1)-C(9) 1.396(3); N(1)-Zn(1)-Cl(1) 110.51(7), N(1)-Zn(1)-Cl(2) 105.16(6), Cl(1)-Zn(1)-Cl(2) 118.08(4), N(1)-Zn(1)-P(1) 82.54(6), Cl(1)-Zn(1)-P(1) 121.01(3), Cl(2)-Zn(1)-P(1) 112.30(3).

3.4 Electrochemistry

The known redox activity of organic phenanthridine derivatives [28] suggested metal complexes containing phenathridine-based ligands might exhibit both metal and ligand-based redox events. Cyclic voltammetry of **2**-**4** was performed in CH_2Cl_2 at ambient temperature (Figure 3). All three complexes showed multiple irreversible events. An irreversible oxidation event at ~ 1.5 V vs Fc/Fc^+ (Fc = (η^5-$C_5H_5)_2Fe$) was common to the voltammograms of **2**-**4** [**2** (Ni): 1.48; **3** (Cu) 1.48; **4** (Zn): 1.65 V]. An irreversible reduction wave at an onset potential negative of -1.5 V was also present in all three voltammograms. That all three complexes exhibit oxidation and reduction events at comparable potentials is consistent with these particular redox events being ligand based [29]. This assignment is also supported by the presence of these waves in cyclic voltammograms of the zinc complex **4**, as metal-based redox events for zinc are inaccessible in the potential window investigated [30]. In addition, (4-diphenylphosphino)phenanthridine (**1**) itself shows irreversible oxidation and reduction events at similar potentials (see Supporting Information, Figure S4), along with an irreversible anodic peak attributed to oxidation of the free phosphine (E_p = 0.76 V vs Fc/Fc^+).

Though the anodic electrochemistry of *mono*(8-diphenylphosphino)quinoline (Ph_2PNqn) complexes of Ni was not reported, the metal-based electrochemical reduction of [*bis*($Ph_2PNqn)_2Ni$][BF_4]$_2$ was observed at -0.66 V vs. Fc/Fc^+ in acetonitrile [31]. No reduction event for **2** is observed at these potentials. For the metal complexes **2** and **3** with

accessible M^n/M^{n-1} reductions, additional cathodic events were observed [**2** (Ni): -2.22; **3** (Cu) -2.26 V]. The cyclic voltammograms of the nickel and copper complexes contain further irreversible oxidation events (**2**: 0.36, 0.88 V; **3**: 0.27, 0.59, 0.84 V) that are assigned as metal-based, in accordance with their absence in the CV of **4**.

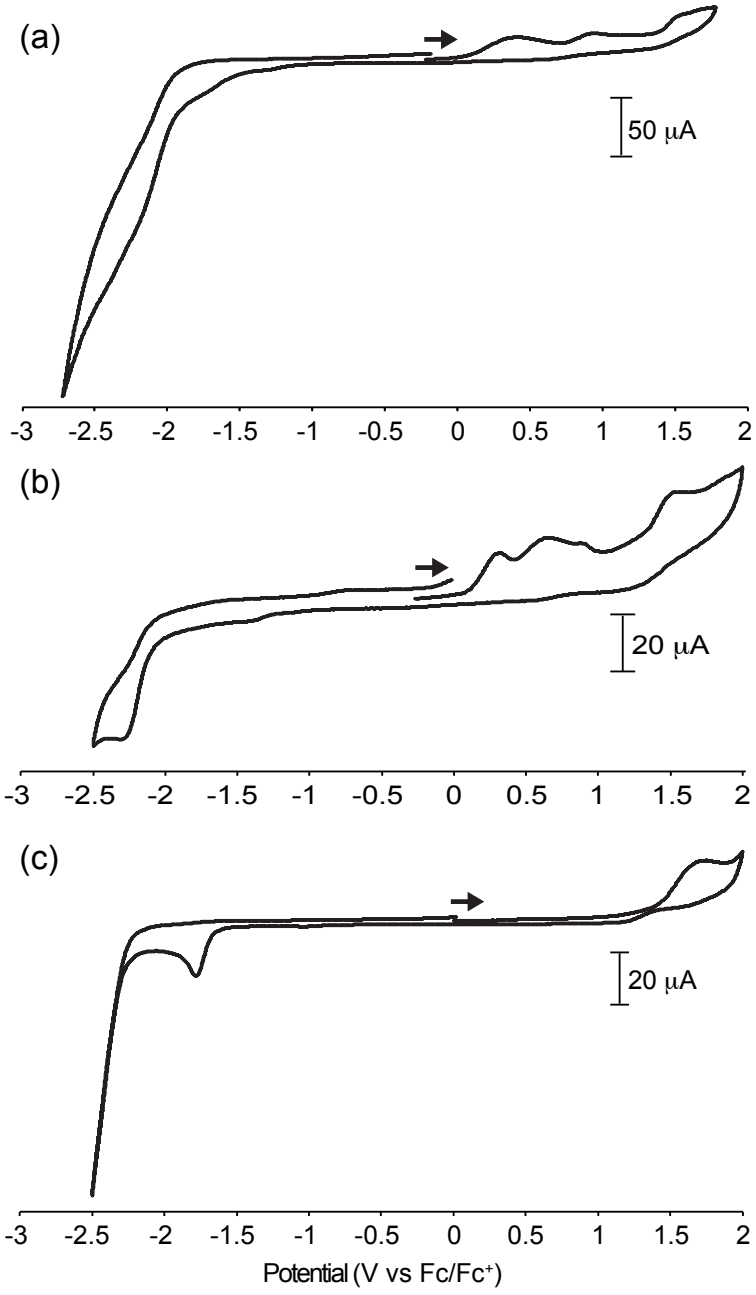


Figure 3. Cyclic voltammograms of **2** (a), **3** (b) and **4** (c) in CH_2Cl_2 at 22 °C at a scan rate of 100 mV/s. Arrows show direction of initial scan. The concentration of analyte was **2** = 1.14×10^{-3} M, **3** = 6.58×10^{-4} M and **4** = 1.33×10^{-3} M respectively, with 0.1 M nBu$_4$NPF$_6$ as supporting electrolyte.

3.5 Emission Spectroscopy

The extended benzo-fused ring system of the phenanthridinyl unit of ligand **1** motivated collection of emission and excitation spectra for complexes **3** and **4** in solution. There is well-established interest in the luminescence of polypyridyl derivatives in bioresponsive imaging [32]. Structurally diverse *N*-heteroaryl-fused phenanthridines in particular have been screened for use as high performance blue-emitting luminophores [28], while receptor ligands based on quinoline have been developed into selective, water-soluble fluorescent 'turn-on' chemosensors for Zn^{2+} [33] and the exciting photoluminescence properties of quinolinyl-supported dinuclear copper(I) halides have been noted [25].

Metal complexes **2**-**4** display rich absorption spectra, with strong features in the UV (230-290 nm, ε = 20 000-90 000 M^{-1} cm^{-1}; Figure 4). The orange-red nickel complex **2** also absorbs in the visible (λ_{max} = 397 nm), while only a weak tail is observed for **3** and solutions of **4** are colorless. Due to solubility limitations, luminescence spectra were collected in a relatively polar solvent (CH_2Cl_2), which typically attenuates luminescence efficiency [34]. Excitation into the lowest energy absorption bands (**3**: $\lambda_{excitation}$ = 380 nm; **4**: $\lambda_{excitation}$ = 360 nm) gives sharp emission peaks at 298 K (**3**: 431 nm; **4**: 382 nm) overlayed with broader features at both higher and lower wavelength (**3**: 456, 406 nm; **4**: 371, 407, 421 nm; Figure 5). As has been observed with *N*-heterocycle-fused phenanthridines [28], there is little overlap of the absorption and fluorescence spectra for phenathridine supported metal complexes **3** and **4**, which could allow for suppression of Förster resonance energy transfer.

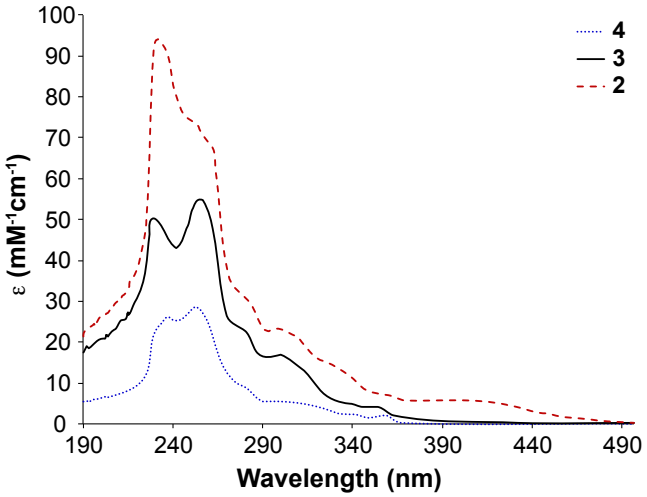


Figure 4. UV-Vis absorption spectra of complexes **2**-**4** in CH_2Cl_2.

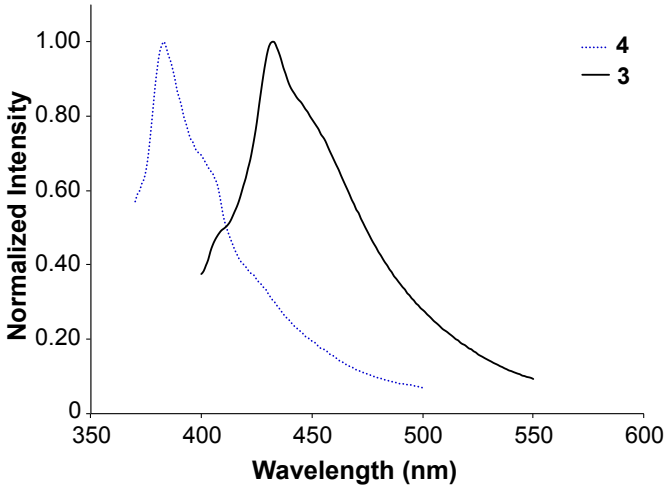


Figure 5. Emission spectra of complexes **3** and **4** in CH_2Cl_2. **3**: $\lambda_{excitation}$ = 380 nm, 5 nm slit width, [**3**] = 1 x 10^{-4} M; **4**: $\lambda_{excitation}$ = 360 nm, 2 nm slit width, [**4**] = 1 x 10^{-4} M.

4. CONCLUSION

A novel heteroleptic chelating ligand, (4-diphenylphosphino)phenanthridine (**1**), bearing a luminescent and electrochemically active phenanthridinyl unit has been prepared and used to support complexes of first row transition metals. X-ray structural analysis of compounds **2**-**4** demonstrates the ability of **1** to accommodate both square planar and tetrahedral geometries. Cyclic voltammograms of complexes of redox-active (Ni, Cu) and redox-inactive metals (Zn) contain similar irreversible features, supporting the redox-active nature of the phenanthridinyl ligand. Both copper and zinc complexes **3** and **4** are emissive in CH_2Cl_2 solution, with emission maxima that range from the visible into the UV. Stabilization of emissive states and alternative complex oxidation states through judicious choice of substituents and ligands to complete the metal coordination spheres, along with in-depth photophysical studies, are currently underway.

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Appendix A. Supplementary Material

CCDC 1422027-1422030 contains the supplementary crystallographic data for **1**, **2**, **3**, and **4**. 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. Supporting information associated with this article

containing excitation spectra for **3** and **4**, and variable temperature ^{1}H NMR spectra for **2** and **3** can be found, in the online version, at http://dx.doi.org/ XX.XXX/XXXXX.

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