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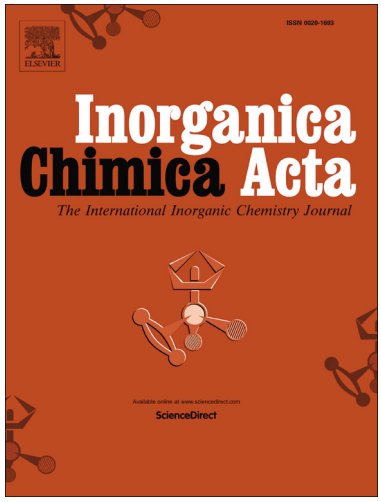

Research paper

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Synthesis of 4-[(2-imidazylethynyl)]-5-(2-pyridylethynyl)veratrole and characterization of the coordination complexes with silver(I) and palladium(II)

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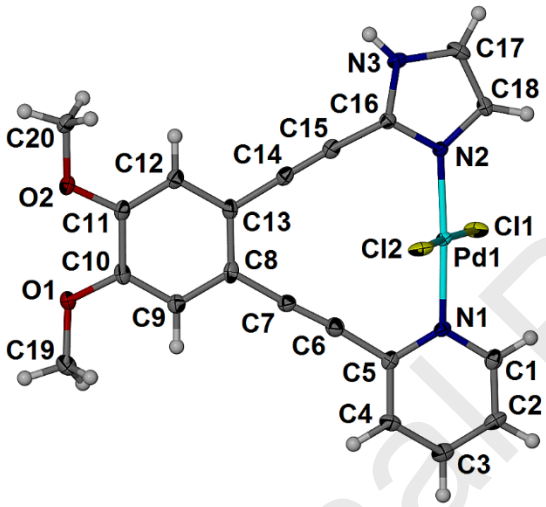
Abstract

We describe the design, synthesis and characterization of the ligand, 4-[(2-imidazylethynyl)]-5-(2-pyridylethynyl)veratrole as well its coordination complexes with silver(I) and palladium(II). ^{1}H NMR titration clearly indicates that 1:1 coordination complexes are formed with both cations. The X-ray structure of the palladium dichloride complex confirms the trans coordination of palladium(II) and the silver trifluoromethanesulfonate complex confirms the linear coordination geometry about silver(I).

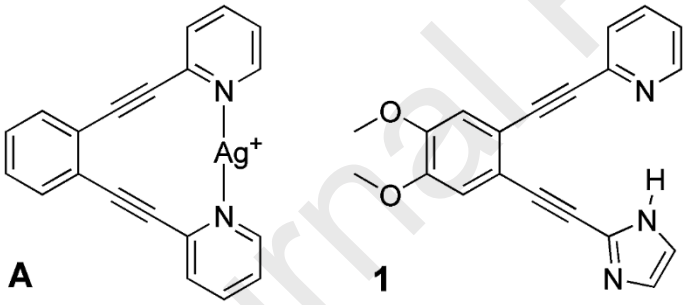


Keywords: Bidentate ligand, coordination complex, palladium(II), silver(I), trans-coordinating, linear coordination

1. Introduction

Pyridines, and to a lesser extent imidazoles, have a rich history of forming coordination complexes with silver(I) and palladium(II) that favor linear and square planar coordination geometries, respectively. One of the enduring motivations for the preparation and study of silver coordination complexes is their potential use in medicinal applications. Indeed, Medici and co-workers recently outlined the ancient history and current potential of silver coordination compounds in the medical field [1]. We have long been interested in the design of bipyridyls that form discrete linear silver(I) coordination complexes and reported the synthesis of a *trans* coordinating bidentate ligand, 1,2-*bis*(2-pyridylethynyl)benzene and its silver(I) and palladium(II) complexes in their favored coordination geometries (linear and square planar respectively) (**A** in Scheme 1) [2]. Thummel and coworkers simultaneously reported the formation of both 1:1 and 2:1 complexes of the same ligand with palladium(II) [3], while Bunz and coworkers reported the related ligand, 4,5-bis(2-pyridylethynyl)veratrole and its coordination chemistry with cobalt(II) chloride, copper(II) acetate and rhodium(II) acetate [4]. More recently, we modified the ligand with heteroatom containing sidearms in the search for enhanced binding to silver(I) cation [5]. It is noteworthy that palladium complexes based on the *trans*-bipyridyl ligand framework and their analogues have been evaluated as catalysts in organic transformations. For instance, 1,2-*bis*(2-pyridylethynyl)benzene palladium(II) complexes were found to be highly efficient catalysts for the Heck reaction [6] and the Suzuki coupling reaction [7], while the oxidative homocoupling of terminal acetylenes in air (Glaser coupling) and the coupling of acid chlorides and alkynes were catalyzed by the palladium(II) complex of 1-(2-pyridylethynyl)-2-(2-thienylethynyl)benzene [8,9]. The analogous *bis* thienyl ligand coupled with $PdCl_2(PPh_3)_2$ was found to catalyze the copper-free Sonogashira coupling reaction of

iodobenzene and alkynes [10]. Interestingly, the synthesis and evaluation of a rotaxane based palladium catalyst in which the palladium was bound to a 1,2-*bis*(2-pyridylethynyl)benzene moiety has been reported [11]. Surprisingly, no related imidazolyl ligands have been reported. We reasoned that a variation of the original ligand including one pyridine and one imidazole moiety would potentially provide access to a neutral silver(I) complex after coordination followed by deprotonation. Given the increasing application of silver, we envisage the need for silver selective ligands that can be modified, and perhaps incorporated on a solid substrate, for use in recovery and extraction and reasoned that the neutral complex would be more stable and have higher potential than a cationic analogue. Herein we describe the synthesis and characterization of the pyridyl-imidazolyl ligand 4-[(2-imidazylethynyl)]-5-(2-pyridylethynyl)veratrole (**1** in Scheme 1) as well its coordination complexes with silver(I) and palladium(II).



Scheme 1

2. Experimental

2.1 Materials

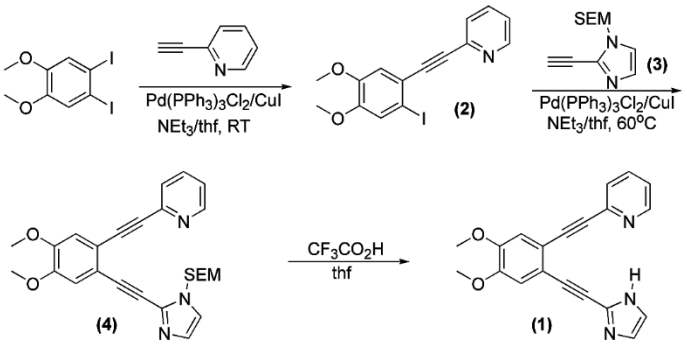
The bulk solvents, hexanes, ethylacetate and dichloromethane used were purchased from Fisher Scientific and used as receivedDichlorobis(triphenylphosphine) palladium (II) was purchased from Pressure Chemical co. Imidazole, 1,2-dimethoxybenzene (veratrole), silver (I) trifluoromethanesulfonate, copper iodide, trifluoroacetic acid, n-butyllithium sodium hydride , triethylamine and tetrahydrofuran were purchased from Sigma Aldrich. 2-Ethynylpyridine was purchased from GFS chemicals. 1-(Trimethylsilyl ethoxy methyl) chloride (SEMCl) was purchased from TCI America. Silver trifluoroacetate and dichlorobis(acetonitrile)palladium II were purchased from Strem chemicals. All chemicals were used as received. Column chromatography was carried out using 230-400 mesh silica gel, purchased from Dynamic Adsorbents, Inc.

^{1}H and ^{13}C NMR spectra were recorded on Varian 400 Unity INOVA spectrometer. All ^{1}H NMR spectra are reported in parts per million (ppm) relative to residual $CHCl_3$ (7.23 ppm) or DMF-d_7 (8.03 ppm). Coupling constants, *J*, are reported in Hertz (Hz). All ^{13}C NMR spectra are reported in ppm relative to residual $CHCl_3$ (77.23 ppm). Elemental analyses were performed by Atlantic Microlabs.

4,5-Diiodoveratrole, [12] 1-[[2-(trimethylsilyl)ethoxy]methyl]-imidazole [13] and 1-[[2-(trimethylsilyl)ethoxy]methyl]-2-iodoimidazole [14] were synthesized as reported.

2.2 Synthesis

The ligand, 4-[(2-imidazoylethynyl)]-5-(2-pyridylethynyl)veratrole, was synthesized by successive Sonogashira coupling reactions followed by deprotection as outlined in Scheme 2.



Scheme 2

2.2.1 Synthesis of 4-iodo-5-(2-ethynylpyridine) veratrole, ***2.***

1,2-Diiodo veratrole (5.00 g, 12.8 mmol), $PdCl_2(PPh_3)_2$ (0.100 g, 0.142 mmol), CuI (92 mg, 0.49 mmol), 2-ethynylpyridine (0.7 ml, 0.660 g, 6.40 mmol), THF (30 mL) and anhydrous triethylamine (10 mL) were reacted under argon atmosphere at room temperature for 4 days. The mixture was diluted with ethyl acetate (200 mL) and washed with water (100 mL x 3) followed by brine (100 mL x 3). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered and solvent removed *in vacuo*. The crude solid was purified by flash column chromatography with a 5:1 mixture of hexane and ethyl acetate as the eluent. The product was obtained as a brown oil which solidified after 2 days (1.44 g, 3.94 mmol, 62%). R_f = 0.27 [EtOAc/hexane (2:1)]. Mp: 89.5–90.1 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, ^3J = 4.8 Hz, 1 H), 7.74 (td, ^3J = 7.8 Hz, ^4J = 2.0 Hz, 1 H), 7.64 (d, ^3J = 7.8 Hz, 1 H), 7.28 (m, 2 H), 7.26 (s, 1 H), 3.90 (s, 3 H), 3.88 ppm (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.5, 149.8, 149.2, 143.2, 136.8, 127.6, 123.1, 121.1, 121.0, 115.6, 92.5, 90.6, 90.2, 56.4, 56.3 ppm. 1,2-Bis(2-pyridylethynyl) veratrole was also isolated as a brown solid (0.612 g, 1.80 mmol, 26%) along with a small amount of unreacted 4,5-diiodoveratrole that was not quantified.

2.2.2 Synthesis of 1-[[2-(trimethylsilyl)ethoxy]methyl]-2-[2 (trimethylsilyl)ethynyl]imidazole

1-[[2-(Trimethylsilyl)ethoxy]methyl]-2-iodoimidazole (2.00 g, 6.17 mmol) and anhydrous triethylamine (15 mL) were added to a pressure flask under argon. $PdCl_2(PPh_3)_2$ (100 mg, 0.142 mmol), CuI (45 mg, 0.24 mmol) and trimethylsilyl acetylene (1.77 g, 2.50 mL, 18.2 mmol) were added under continuous argon flow. After 5 minutes the argon flow was stopped and the pressure flask sealed. The reaction was heated to 60 ˚C for 40 h and then cooled to room temperature. The solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2 (100 mL). The organic layers was washed with brine (80 mL x 2) and subsequently dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the crude product purified by flash column chromatography with a mixture of 20:1 hexane and ethyl acetate as the eluent. After purification, the product was obtained as a yellow oil (0.812 g, 44%). R_f = 0.3 [EtOAc/hexane (2:1)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (d, ^3J = 3.2 Hz, 2 H), 5.34 (s, 2 H), 3.43 (t, ^3J = 8.4 Hz, 2 H), 0.87 (t, ^3J = 8.4 Hz, 2 H), - 0.12 (s, 9 H), -0.06 ppm (s, 9 H).

2.2.3 Synthesis of 1-{[2-(trimethylsilyl)ethoxy]methyl}-2-ethynylimidazole, ***3.***

A solution of potassium hydroxide (300 mg, 5.35 mmol) in water (0.5 mL) was added to a solution of 1-[[2-(trimethylsilyl)ethoxy]methyl]-2-[2 (trimethylsilyl)ethynyl]imidazole (0.810 g, 2.72 mmol) in ethanol (10 mL). The mixture was stirred at room temperature and the reaction monitored by TLC. After 2 h, the solvent was evaporated, and the residue dissolved in CH_2Cl_2 (60 mL), washed with brine (50 mL x 2) and dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo* and the crude product purified by flash column chromatography with a mixture of 10:1 hexane and ethyl acetate as the eluent. Upon purification, the product was obtained as a yellow oil (0.390 g, 65%). R_f = 0.3 [hexane/EtOAc (2:1)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (d, ^3J = 3.2 Hz, 2 H), 5.37 (s, 2 H), 3.50 (t, ^3J = 8.4 Hz, 2 H), 3.32 (s, 1 H), 0.87

(t, ^{3}J = 8.4 Hz, 2 H), -0.06 ppm (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.1, 130.1, 120.5, 81.5, 75.2, 72.9, 66.5, 17.6, -1.5 ppm.

*2.2.4 Synthesis of 4-[1-(2-trimethylsilylethoxymethyl)]-1H-imidazylethynyl [5-(2pyridylethynyl)] veratrole, **4***

Compound **3** (410 mg, 1.85 mmol) and compound **2**, (1.24 g, 3.38 mmol) were reacted in anhydrous triethylamine (3 mL) and anhydrous THF (5 mL) with $PdCl_2(PPh_3)_2$ (100 mg, 0.142 mmol) and CuI (45 mg, 0.24 mmol) as the catalyst under argon at 60 ˚C for 24 h. The mixture was cooled to room temperature, diluted with CH_2Cl_2 (100 mL) and washed with brine (50 mL x 2). The organic layer was separated, dried over anhydrous Na_2SO_4, and solvent removed *in vacuo*. The crude product was purified by flash column chromatography with a 1:1 mixture of hexane and ethyl acetate as the eluent. The product, **4**, was obtained as a red oil, which solidified after 5 days (390 mg, 46%). R_f = 0.30 [EtOAc/hexane (2:1)]. Mp: 110.8–111.9 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, ^{3}J = 4.8 Hz, 1 H), 7.66 (td, ^{3}J = 7.8 Hz, ^{4}J = 2.0, Hz, 1 H), 7. 55 (d, ^{3}J = 7.8 Hz, 1 H), 7.23 (ddd, ^{3}J = 7.8 Hz, ^{4}J = 5.0 Hz , ^{5}J = 1.2 Hz, 1 H), 7.18 (s, 1 H), 7.08 (d, ^{3}J = 1.2 Hz, 3 H), 5.52 (s, 2 H), 3.89 (s, 6 H, OCH_3), 3.49 (t, ^{3}J = 8.4Hz, 2 H), 0.76 (t, ^{3}J = 8.4 Hz, 2 H), -0.15 ppm (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 149.8, 149.7, 143.3, 136.3, 132.5, 130.7, 127.3, 123.0, 120.3, 117.7, 117.6, 114.7, 114.3, 91.7, 91.6, 88.1, 81.5, 75.6, 66.6, 56.2, 17.7, -1.4 ppm. Anal. Calcd. for $C_{26}H_{29}N_3O_3Si$: C, 67.94; H, 6.36; N, 9.14. Found: C, 65.85; H, 6.13; N, 8.82.

*2.2.5 Synthesis of 4-[(2-imidazylethynyl)]-5-(2-pyridylethynyl) veratrole, **1***

Trifluoroacetic acid (4.3 mL) was added to a solution of **12** (100 mg, 0.27 mmol) in THF (0.6 mL). The mixture was stirred at room temperature and monitored by TLC. After 7 h the

trifluoroacetic acid was removed *in vacuo* and the crude product dissolved in CH_2Cl_2 (50 mL). The solution was stirred with a saturated solution of $NaHCO_3$ (10 mL) and the organic layer was separated, washed with brine (40 mL), and dried over anhydrous Na_2SO_4. The solvent was again removed *in vacuo* and the crude product was purified by preparative-TLC with a 5:1 mixture of ethyl acetate/ hexane (R_f = 0.45). After purification, the product was isolated as a brown solid (36 mg, 0.11 mmol, 50%) and recrystallized from a 1:1 mixture of acetonitrile and dichloromethane to afford brown crystals suitable for x-ray determination. The reaction was repeated multiple times in an attempt to improve the overall yield. Mp: 185.1–186.9 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, ^3J = 4.4 Hz, 1 H), 7.74 (td, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 1 H), 7. 55 (d, ^3J = 7.8 Hz, 1 H), 7.30 (ddd, ^3J = 7.6 Hz, ^{4}J = 4.8 Hz, ^5J = 1.2 Hz, 1 H), 7.15 (s, 2 H), 7.02 (d, ^3J = 2.0 Hz, 2 H), 3.90 (s, 3 H), 3.89 ppm (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 149.4, 149.2, 143.0, 137.3, 131.0, 127.2, 123.2, 120.1, 118.0, 113.5, 112.6, 91.8, 90.0, 89.0, 85.4, 56.3 ppm. Anal. Calcd. for $C_{20}H_{15}N_3O_2$: C, 72.94; H, 4.59; N, 12.76. Found: C, 72.74; H, 4.52; N, 12.63.

2.2.7 Synthesis of {4-[(2-imidazylethynyl)]-5-(2-pyridylethynyl) veratrole} palladium (II) dichloride

The ligand, **1** (3 mg, 0.0091 mmol) was dissolved in anhydrous CH_3CN (2 mL), and the solution was added to a separate solution of $PdCl_2(CH_3CN)_2$ (0.0024 g, 0.0091 mmol) in CH_3CN (0.3 mL) in a vial. The vial was capped and placed in the hood. Orange crystals were harvested after 5 days (2.2 mg, 54 %). Analysis was performed on the accumulated product obtained from several similar experiments. ^{1}H NMR (400 MHz, DMF-d_7): δ 15.86 (br, 1H), 8.87 (d, ^3J = 7.8 Hz, 1 H), 8.06 (td, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 1 H), 7. 87 (d, ^3J = 7.8 Hz, 1 H), 7.62–7.60 (m, 1 H), 7.56–7.52(m, 2H) 7.27 (t, ^3J = 1.56 Hz, 1 H), 7.24 (s, 1 H), 4.03 (s, 3H, OCH_3), 4.02 ppm (s, 3H,

OCH_3). Anal. Calcd. for $C_{20}H_{15}Cl_2N_3O_2Pd$: C, 47.41; H, 2.98; N, 8.29. Found: C, 47.26; H, 3.14; N, 8.49.

2.2.8 Synthesis of {4-[(2-imidazylethynyl)]-5-(2-pyridylethynyl) veratrole} silver (I) trifluoroacetate

The ligand, **1** (3 mg, 0.0091 mmol) was dissolved in anhydrous CH_3CN (2 mL), and the solution was added to a separate solution of $_2CF_3CO_2Ag$ (0.0024 g, 0.0091 mmol) in CH_3CN (0.3 mL) in a vial. 1 mL each of ethanol and dichloromethane were added. The vial was capped and placed in the freezer. Colourless crystals were harvested after 7 days (1.8 mg, 35 %). Analysis was performed on the accumulated product obtained from several similar experiments. ^{1}H NMR (400 MHz, DMF-d_7): δ 8.87 (d, ^3J = 7.8 Hz, 1 H), 8.26 (td, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 1 H), 8.05 (m, 1 H), 7. 79 (ddd, ^3J = 7.8 Hz, ^4J = 5.1 Hz, ^5J = 1.6 Hz, 1 H), 7.71 (s, 1 H), 7.54 (s, 1H), 7.29 (s, 1 H), 7.19 (s, 1 H), 3.94 (s, 3H, OCH_3), 3.93 ppm (s, 3H, OCH_3). Anal. Calcd. for $C_{22}H_{15}AgF_3N_3O_4.H_2O$: C, 46.50; H, 3.02; N, 7.39. Found: C, 46.59; H, 2.87; N, 7.13.

2.3 Titrations.

*2.3.1 Titration of ligand **1** with silver(I) triflate*

A solution of ligand **1** (9 mg, 0.027 mmol) in DMF-d_7 (0.9 mL, 30.36 mM) was carefully transferred into a clean and dry NMR tube and the ^{1}H NMR spectrum recorded. A stock solution of CF_3SO_3Ag was then prepared in a vial by dissolving CF_3SO_3Ag (78 mg, 0.30 mmol) in DMF-d_7 (0.9 mL, 337.29 mM). The titration begun with addition of a 10 µL aliquot of the CF_3SO_3Ag solution to the solution of the ligand. The mixture was vortexed to ensure homogeneity and the ^{1}H NMR spectrum recorded. The procedure was repeated with subsequent aliquots of 10 µL of

CF_3SO_3Ag and collecting ^1H NMR spectra until a total of 150 µL of the silver triflate was added. At this stage larger aliquots were added until 5 eq. of CF_3SO_3Ag was added.

*2.3.2 Titration of ligand **13** with bis(acetonitrile)palladium(II) dichloride*

A solution of ligand **1** (23 mg, 0.068 mmol) in DMF-d_7 (0.9 mL, 75.71 mM) was carefully transferred into a clean and dry NMR tube and the ^1H NMR spectrum of the ligand recorded. A stock solution of $PdCl_2(CH_3CN)_2$ was prepared in a vial by dissolving $PdCl_2(CH_3CN)_2$ (78 mg, 0.30 mmol) in DMF-d_7 (0.9 mL, 759.04 mM). The titration began on addition of a 20 µL aliquot of the $PdCl_2(CH_3CN)_2$ stock solution to the solution of **1**. The mixture was vortexed to ensure homogeneity and the ^1H NMR spectrum recorded. Injection of 20 µL into the tube and collection of ^1H NMR spectrum continued until proton peaks associated with the ligand protons completely disappeared (100 µL added in total).

2.4 Crystallography

For each sample, a single crystal was mounted on a Kryoloop using viscous hydrocarbon oil. Data were collected using a Bruker Apex 2 CCD diffractometer equipped with Mo Kα radiation with λ = 0.71073 Å. Data collection at low temperature was facilitated by the use of a Kryoflex system with an accuracy of ±2 K. Initial data processing was carried out using the Apex 3 software suite [15]. Structures were solved by direct methods using SHELXT-2018 [16] and refined against F^2 using SHELXL-2018 [17]. The program X-Seed was used as a graphical interface [18]. All H atoms were located in the difference maps. The hydrogen atom on the imidazole N in both structures was restrained in the refinement with N—H = 0.88 (2) Å with $U_{iso}(H) = 1.2U_{eq}(N)$. All other hydrogen atoms were treated as riding atoms in geometrically idealized positions with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aryl protons and C—H =

0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl protons. For complex **1**·$PdCl_2$, the program PLATON SQUEEZE was used to ameliorate the negative effect on highly disordered solvent on the refinement [19]. Several crystals of the complex **1.**$AgCF_3CO_2$ were also selected for X-ray analysis, however, these were very weak diffractors with multiple silver centers and high disorder and did not lead to reasonably refined data. Subsequently, data was collected from multiple crystals of the complex **1**·$AgCF_3SO_3$ prepared in a similar way and also culled from titration experiments. These crystals were also weakly diffracting even with extended time of data collection. The result presented here corresponds to the best data obtained. The structure of the complex **1**·$AgCF_3SO_3$ included four unique coordination complexes in the unit cell. Two of the four coordination complexes were readily refined. On the contrary, the third and fourth complexes required repeated refinement with the aid of multiple restraints (DFIX, DANG, EADP, FLAT and SIMU). While it was apparent that the ligands are disordered with respect to the interchange of the imidazole and pyridine moieties, this was not modeled given the complexity of the refinement. Two of the triflate anions were also refined with the aid of multiple restraints. We were unable to adequately model and refine two triflate anions and the presence of disordered solvent was also suspected. Consequently, the program SQUEEZE run through the Platon interface was used to facilitate refinement.

3. Results and discussion

3.1 Ligand Synthesis and Characterization

The ligand was synthesized in moderate overall yield starting from 4,5-diiodoveratrole. The synthesis began with the Sonogashira coupling of 2-ethynylpyridine with 4,5-diiodoveratrole in triethylamine, catalyzed by bis(triphenylphosphine)palladium(II) dichloride and copper(I) iodide to form 4-iodo-5-(2-ethynylpyridine) veratrole, **2**, **in 62% yield** along with

the disubstituted pyridyl product, 1,2-Bis(2-pyridylethynyl) veratrole **in 26%** and a small amount of 4,5-diiodoveratrole. The synthesis of the second moiety began with protection of imidazole with the trimethylsilylethyoxymethyl group (SEM) [13], followed by iodination according to the procedure described by Knapp [14]. Subsequent Sonogashira coupling with trimethylsilylacetylene followed by base promoted deprotection of the alkyne provided alkyne **3** in relatively low yield, 29 % overall for the two steps, possibly due to the solubility of the product in water and difficulty monitoring the reactions. The alkyne **3** was then coupled with 4-iodo-5-(2-ethynylpyridine) veratrole, **2** using standard Sonogashira coupling reaction conditions. Several attempts were made to improve the yield that resulted in the modest yield of **4** (46 %) after reaction at 60 ^{o}C for 24 h. The coupled SEM-protected imidazole product was deprotected with trifluoroacetic acid to yield the desired ligand. The ^{1}H NMR of the ligand clearly established the presence of protons unique to each of the three aromatic rings and further characterization by ^{13}C NMR (see Figure S1-S3), elemental analysis and single crystal X-ray crystallography confirmed the structure.

The single crystal X-ray structure of **1** shown in Figure 1 contains a single molecule in its asymmetric unit with an intramolecular hydrogen bond with distances H2N---N1 and N2---N1 1.97(2) and 2.872(4) Å respectively with angle N1---H2N-N2 of 167(3)°. The imidazole ring is essentially coplanar with the benzene ring with interplanar dihedral angle of 2.11(5)° although the pyridyl ring is slightly twisted with respect to the benzene ring with a dihedral angle of 15.00(8)°. The ethynyl bond to the imidazole is slightly distorted from linearity to accommodate the intramolecular hydrogen bond with C(13)-C(14)-C(15) and C(14)-C(15)-C(16) angles of 172.8(3) and 172.8(3)° respectively (Table 2). The molecules of **1** form of planar sheets where adjacent molecules interact through C-H---N and C-H---O interactions (see Table 3).

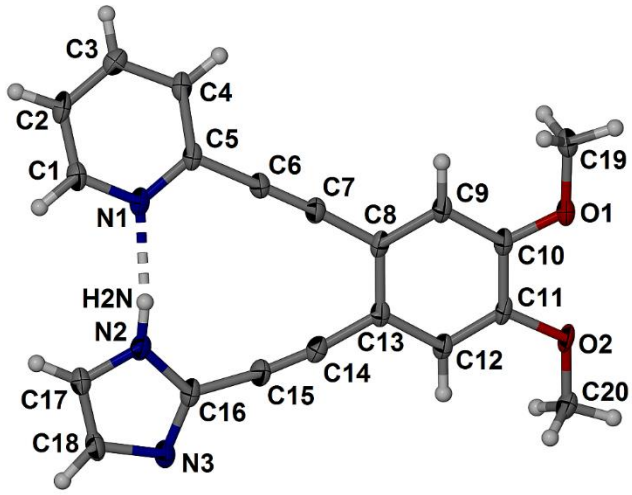


Figure 1. The labelled asymmetric unit of ligand, **1** with displacement ellipsoids drawn at the 50% level and the intramolecular hydrogen bond shown as a dashed line.

3.2 ^{1}H NMR studies of metal complexation

Binding of silver(I) salts by 1,2-bis(2′-pyridinylethynyl)benzenes [5] and related bipyridyl ligands [20] is characterized by rapid exchange between complexed and un-complexed ligands that is significantly faster than the time scale of the NMR measurement. Consequently, the observed NMR spectrum is a weighted average spectrum of bound and unbound ligand rather than distinct peaks corresponding to bound and unbound ligand. Therefore the proton chemical shift of the pyridine protons gradually shift downfield as increments of Ag(I) are added until no further chemical shift change is observed [5,20]. The incremental addition of silver(I) triflate to a 0.03 M solution of ligand **1** in dimethylformamide-d_7 demonstrates the change in chemical shift of the pyridyl protons as shown in Figure 2. It is clear that after addition of 1 equivalent of silver(I), at this concentration, there was no further change in the chemical shift of the ligand protons thereby indicating the formation of a 1:1 ligand:silver(I) complex in solution at this

concentration. It is noteworthy that the imidazole N-H proton is broadened and is shifted downfield in the NMR spectrum. Thus, under these conditions, the ligand is not deprotonated after forming the coordination complex with silver(I).

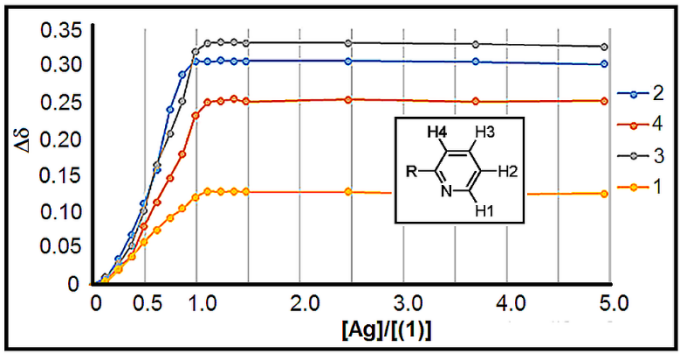


Figure 2. Spectral changes observed on incremental addition of silver(I) trifluoromethane sulfonate into a DMF-d_7 solution of ligand **13** (0.03 mM).

In contrast, the complexation of palladium(II) salts by 1,2-bis(2′ pyridinylethynyl)benzenes and related bipyridyl ligands revealed that binding of Pd(II) was slow on the NMR time scale. Accordingly, proton signals for both the bound ligand and the unbound ligand are observed in solutions where only a portion of the ligand is bound [20]. The results of the titration of ligand, **1,** with bis(acetonitrile)palladium(II) dichloride is shown in Figure 3. It is noteworthy that the signal for un-complexed ligand completely disappeared after addition of 1.0 equiv. of Pd(II), thereby confirming the formation of a 1:1 complex in solution (Figure 3).

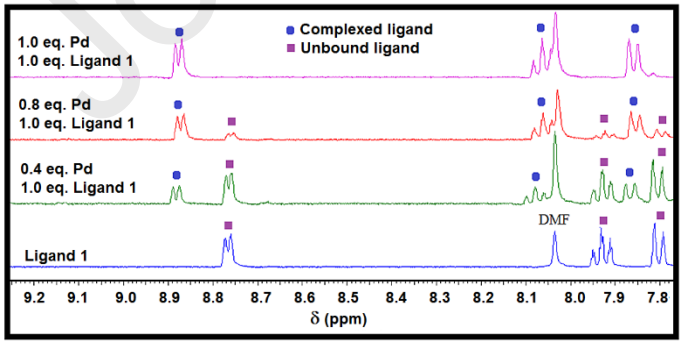


Figure 3. Stacked ^{1}H NMR spectra obtained on sequential addition of $PdCl_2(CH_3CN)_2$ into a 0.076M DMF-d_7 solution of **1**.

3.3 X-ray crystallographic studies of metal complexation

The palladium complex **1**·$PdCl_2$ crystallized from an equimolar solution of **1** and $PdCl_2(CH_3CN)_2$ in acetonitrile in the monoclinic space group $P2_1/c$ as orange blocks. In the complex, the ligand is essentially planar with dihedral angles of 2.35(2) and 1.69(18)° between the benzene ring and the pyridine and imidazole rings respectively (Figure 4). The palladium has square planar coordination geometry with N1-Pd1-N2 and Cl1-Pd1-Cl2 angles of 176.86(12) and 174.40(4)° respectively and N-Pd-Cl angles between 89.28(9) and 91.06(9)°. The imidazole N-H has a close contact to a chloride from an adjacent complex with an H---Cl distance of 2.42(3)Å that is 80% of the sum of the Vander Waals radii [21].

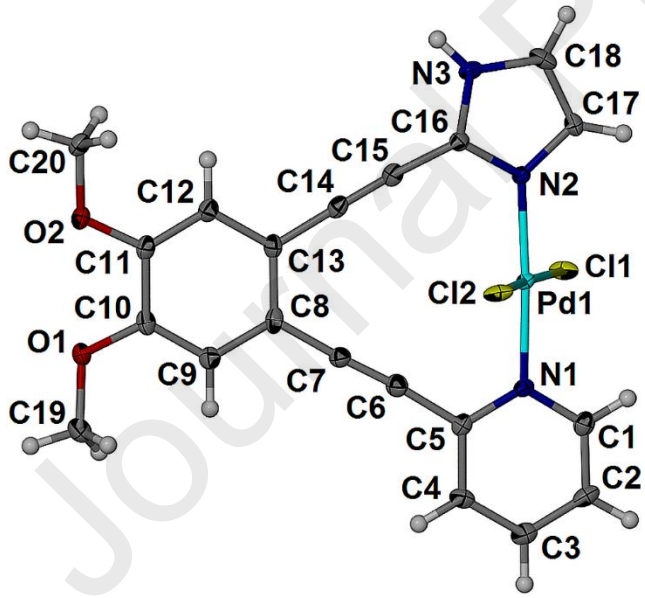


Figure 4. View of the palladium coordination complex with ligand **(1)** showing the atom labeling with displacement ellipsoids drawn at the 50% level.

The 1:1 silver(I) triflate complex crystallized in the monoclinic space group Cc. However, the unit cell contained 4 unique silver complexes with triflate counterions. Of these 4 complexes, two were severely disordered, as shown in Figure 5, as were all four triflate anions. In addition, the ligand complexes all exhibited some level of positional disorder between the imidazole and pyridyl rings. Refinement of the structure was only successful when the two most highly disordered triflate anions and the disordered incorporated solvent were removed using the program SQUEEZE run through the Platon interface. Subsequent refinement was performed with multiple restraints as described in the experimental section. Despite the fact that the final refinement is below generally accepted expectations for publication, it does confirm the coordination mode of the ligand. While the Ag-N bond distances and the N-Ag-N angles, collected in Table 4, are typical for pyridyl and imidazolyl silver complexes, it should be noted that positional disorder in all four complexes and the use of restraints is expected to have affected these values. Nevertheless, it is clear that the ligand does indeed bind silver(I) cations in an intramolecular linear mode similar to the related dipyridyl ligand.

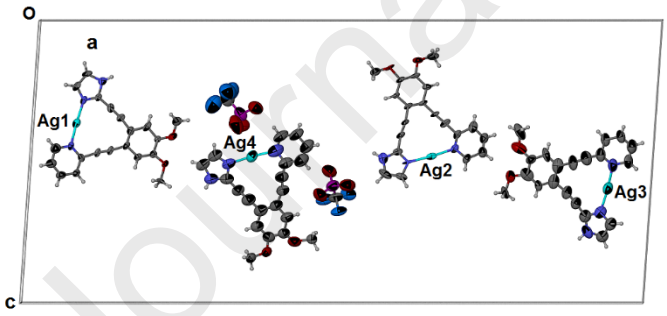


Figure 5. View of the asymmetric unit of the silver(I) coordination complex with ligand, **1** with the unique silver atoms labeled and displacement ellipsoids drawn at the 50% level.

The program SQUEEZE reported 8 distinct void spaces in the unit cell after removal of the two highly disordered triflates and disordered solvent from the refinement. Given that the unit cell contains a total of 16 silver complexes, 4 per asymmetric unit, and, with 2 triflates from the asymmetric unit modelled in the refinement, each of these 8 void spaces reasonably contain a triflate anion with an electron count of 73. Four of these voids have SQUEEZEd electron count of 84 electrons and the other 4 have a SQUEEZEd electron count of 112 electrons. The smaller void likely also includes a water molecule, for a total electron count of 83, while the larger voids must contain a disordered triflate and a solvent molecule such as dichloromethane with a total electron count of 115. A view of the complexes stacked along the b-axis, as shown in Figure S12 reveals the two distinct void spaces with different volumes.

4. Conclusions

In summary, we reveal the first synthesis of a trans coordinating ditopic ligand containing both pyridyl and imidazolyl moieties and characterization of its coordination to both silver(I) and palladium(II) cations. ^{1}H NMR studies confirm the 1:1 stoichiometry between the ligand and the silver and palladium cations respectively. X-ray studies confirms the *trans* coordination of palladium(II) cation to form a square planar complex and the linear coordination of silver(I) by the pyridyl and imidazolyl moieties. Our future studies will focus on improving the synthesis of this, and related, imidazolyl ligands with a goal of forming neutral coordination complexes and exploring their potential uses.

5. Acknowledgment

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Table 1. Crystallographic data for compound **1** and complex **1.**$PdCl_2$

	Compound **1**	Complex **1.**$PdCl_2$	Complex **1.**$Ag(CF_3SO_3)$
Formula	$C_{20}H_{15}N_3O_2$	$C_{20}H_{15}Cl_2N_3O_2Pd$	$C_{20}H_{15}AgF_3N_3O_2S$
Formula weight	329.35	506.65	526.28
Crystal dim. (mm^3)	0.25 x 0.21 x 0.02	0.20 x 0.15 x 0.02	0.40 x 0.10 x 0.05
Crystal system	Triclinic	Monoclinic	Monoclinic
Crystal color	Colorless	Gold	Colorless
Space group	*P*-1	P 2_1/c	Cc
a (Å)	6.698 (3)	11.1420 (7)	53.94(2)
b (Å)	9.659 (4)	27.3615 (17)	6.826(3)
c (Å)	13.379 (6)	7.4271 (5)	24.457(9)
α (deg)	110.387 (6)	90	90
β (deg)	95.185 (6)	95.878 (1)	93.972
γ (deg)	92.835 (7)	90	90
Z	2	4	16
V ($Å^3$)	804.9 (6)	2252.3 (3)	8983 (6)
ρ_{calcd} (mg m^{-3})	1.359	1.494	1.557
T (K)	100 (2)	100 (2)	10 (2)
μ (mm^{-1})	0.090	1.080	1.035
Measured, independent & observed reflections	10255/3575/1868	28387/5037/4568	50289/19753/10759
Data/ parameters/restraints	3575/232/1	5037/259/1	19753/1061/817
R_{int}	0.059	0.041	0.114
Goodness of fit	0.992	1.147	1.044
R1/wR2	0.065/0.165	0.045/0.102	0.116/0.335
R1/wR2 (all data)	0.128/0.207	0.050/ 0.102	0.181/0.335
CCDC	1956600	1956601	1960422

Table 2. Selected bond lengths [Å] and angles [°] for compound **1** and complex **1.**$PdCl_2$

Bond length		**Bond angle**	
Compound 1			
C6-C7	1.198(4)	C5-C6-C7	178.7(3)
C14-C15	1.200(4)	C6-C7-C8	174.4(3)
		C14-C15-C16	172.8(3)
		C15-C16-C17	172.8(3)
Complex 1.$PdCl_2$			
Pd1-N1	2.018(3)	N1-Pd1-N2	176.86(12)
Pd1-N2	2.006(3)	Cl1-Pd1-Cl2	174.40(4)
Pd1-Cl1	2.3335(10)	N1-Pd1-Cl1	90.41(9)
Pd1-Cl2	2.3185(9)	N1-Pd1-Cl2	89.28(9)
C6-C7	1.197(5)	N2-Pd1-Cl1	89.56(9)
C14-C15	1.201(5)	N2-Pd1-Cl2	91.06(9)

Table 3. Hydrogen bond geometry [Å, °] for compound **1**

D-H---A	**D-H**	**H---A**	**D---A**	**D-H---A**
N2-H2N---N1	0.92(2)	1.97(2)	2.872(4)	167(3)
C2-H2---O1^{i}	0.95	2.38	3.303(4)	164
C9-H9---N3^{ii}	0.95	2.43	3.369(4)	168

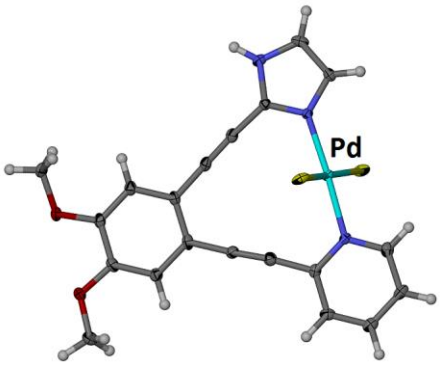
Symmetry codes: (i) *x*, *y*, *z*+1; (ii) *x*, *y*+1, *z*.

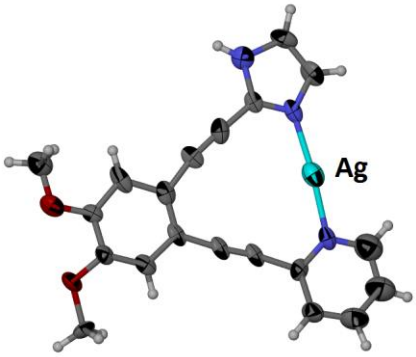
Table 4. Selected bond lengths [Å] and angles [°] for complex **1.**Ag($CF_3SO_{3)}$

Bond length				**Bond angle**	
Ag1-N1	2.059(17)	Ag1-N2	2.098(18)	N1-Ag1-N2	173.6(6)
Ag2-N4	2.14(2)	Ag2-N5	2.073(19)	N4-Ag2-N5	174.9(6)
Ag3-N7	2.09(3)	Ag3-N8	2.19(3)	N7-Ag3-N8	174(1)
Ag4-N10	2.13(2)	Ag4-N11	2.15(4)	N10-Ag4-N11	174(1)

Highlights

- Synthesis and characterization of a trans-coordinating ligand including one pyridine and one imidazole moiety.
- NMR studies of silver(I) and palladium(II coordination by the pyridyl-imidazolyl ligand.
- X-ray structural characterization of linear coordination of Ag(I) and trans-coordination of Pd(II).





Author Contribution Statement

Eric Bosch:
Conceptualization, Data curation, Methodology, Validation, Formal analysis, Funding acquisition, Investigation, Visualization, Writing- Original draft, Project administration, Resources, Software, Supervision.

Chideraa I. Nwachukwu:
Methodology, Investigation, Validation, Data curation, Visualization, Writing –review & editing.