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Article

A New Totally Flat N(sp^2)C(sp^2)N(sp^2) Pincer Palladacycle: Synthesis and Photoluminescent Properties

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The Sonogashira coupling of 2-bromopyridine with 8-quinolinyl-acetylene affords 2-pyridinyl-8-quinolinyl-acetylene (**1**) in high yields. The chloropalladation of **1** with Li_2PdCl_4 in methanol at room temperature affords the pincer palladacycle (C_5H_4N-2-C=C(Cl)-8-$C_9H_6\kappa N,\kappa C,\kappa N$)PdCl (**2**) in 63% yield. The X-ray molecular structure of (**2**) shows that it is totally flat and that it is associated in pairs though π-stacking between alternate pyridine–quinoline moieties (3.448 Å). The pairs are also connected by π-stacking with an interpair distance of 3.452 Å between quinoline–quinoline moieties. A very low fluorescence emission was also revealed by the pincer palladacycle **2** in both solution and the solid state, which has been ascribed to an excimeric emission due to the particular structure (rigid and totally flat) of **2** in the solid state.

Introduction

Pincer type palladacycles are one of the most popular and investigated classes of cyclometalated compounds.[1,2] The possibility of fine-tuning the steric and electronic properties of the metal center by simply changing the donor groups or their substituents in the anionic six-electron donor ligand confers to this class of compounds a plethora of applications.[3] These compounds have been used as efficient catalyst precursors for C−C coupling reactions,[4] and as “molecular” materials for crystalline switches, sensors,[5] etc. In particular, light-emitting NNC and NCN pincer type palladacycles (Figure 1), obtained mainly from the metalation of 6-aryl-2,2′-bipyridines ligands, are potential candidates for optical luminescent devices.[6] However, with rare exceptions, reasonable luminescence of these compounds is only observed in a glass matrix at 77 K. The solid state luminescence at room temperature has been reported only recently for the nearly flat palladated 6-carboxyl-2,2′-bipyridine compound.[6a] The observed solid state luminescence has been ascribed to an excimeric emission. The C−H bond activation methods used,

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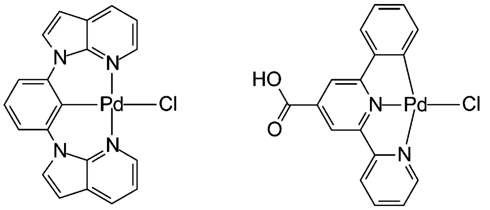

Figure 1. Examples of pincer NCN and NNC pincer palladacycles that display luminescent properties.

in most of the cases, for the preparation of these potential light-emitting palladacycles are almost restricted to those containing Pd−aryl bonds.

We have recently reported that the trans-chloropalladation of heterosubstituted alkynes is an effective method for preparing various types of pincer palladacycles.[7] We envisaged that this method could be used for the construction of palladacycles containing pyridine-type ligands. We wish to report that this method can indeed be used for the construction of a "rigid" and totally flat compound containing pyridine and quinoline ligands that displays luminescence properties in both solution and the solid state at room temperature.

Experimental Section

General Methods. All reactions involving organometallic compounds were carried out under argon or nitrogen atmosphere in oven dried Schlenk tubes. Solvents were dried with suitable drying agents and distilled under argon prior to use. The alkyne **5** was prepared in 85% yield using a published method.[8] All the other chemicals were purchased from commercial sources (Acros or Aldrich) and used without further purification. Elemental analyses were performed by the Analytical Central Service of IQ-USP (Brazil). NMR spectra were recorded on a Varian Inova 300 spectrometer. Infrared spectra were performed on a Bomem B-102 spectrometer. Gas chromatography analyses were performed with a Hewlett-Packard-5890 gas chromatograph with a FID and 30 m capillary column with a dimethylpolysiloxane stationary phase. Mass spectra were obtained using a GC/MS Shimadzu QP-5050 (EI, 70 eV). UV−vis absorption spectra were taken on a Cary 50 Varian spectrophotometer or a Shimadzu, model UV-1601PC. Solid state and solution fluorescence spectra were measured with a Hitachi spectrophotometer model F-4500. The experiments in solution were performed at room temperature in a concentration of 10^{-5} M.

X-ray Structures Analyses of 2. Crystals of **2** were first prepared by slow diffusion of hexane into an acetone solution. However, these crystals suffered from loss of solvent and were recrystallized from CH_2Cl_2 by very slow solvent evaporation. A crystal was mounted on a glass fiber with perfluoropolyether. The measurement was made on a Bruker SMART-CCD diffractometer with graphite monochromated Mo Kα radiation. Frames corresponding to a sphere of data were collected using the ω-scan technique, and 20 s exposures of 0.3° in ω were taken. An absorption correction was applied using SADABS[9] based on the Laue symmetry of the reciprocal space; the data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques, all non-hydrogen atoms were refined with anisotropic displacement parameters, the hydrogen atoms could be located in the Fourier map, and all hydrogen atoms were considered at calculated positions. Half a molecule of CH_2Cl_2 was located per one molecule of the palladium compound (special position on a 2-fold symmetry axis). The full-matrix least-squares refinement against F^2 converged. All calculations were performed using the SHELXTL crystallographic software package of Bruker.[10]

Synthesis of 8-Quinolinyl-acetylene. A mixture of 8-bromoquinoline (3.00 g, 14.4 mmol), trimethylsilyl-acetylene (1.86 g, 19.0 mmol), $Pd(PPh_3)_2Cl_2$ (20 mg), cuprous iodide (20 mg), and triphenylphosphine (70 mg) was suspended in triethylamine (20 mL), and the resulting suspension was stirred and heated at 90 °C for 1.5 h. The reaction mixture was quenched with aqueous sodium carbonate solution (10%, 20 mL) and was extracted with ether (2 × 15 mL). The solvent of the combined organic extract was evaporated under reduced pressure, and the resulting oily residue, redissolved in methanol (20 mL), was treated with potassium fluoride (1.74 g, 30 mmol) and stirred at room temperature for 1.5 h. Evaporation of the solvent and chromatographic purification (silica gel column, hexanes/EtOAc = 1/1) afforded a brown oil (1.20 g, 54% yield), that solidified in the refrigerator. CG-MS (*m*/*z*, rel int, peak): 153, 100, $M^{+\bullet}$; 126, 30, $[M - HCN]^{+\bullet}$. ^1H NMR ($CDCl_3$): δ 9.06 (dd, 1H, CH arom, $^3J_{HH} = 4.3$ Hz and $^4J_{HH} = 1.7$ Hz); 8.15 (dd, 1H, CH arom, $^3J_{HH} = 8.3$ Hz and $^4J_{HH} = 1.7$ Hz); 7.96 (dd, 1H, CH arom, $^3J_{HH} = 7.2$ Hz and $^4J_{HH} = 1.5$ Hz); 7.81 (dd, 1H, CH arom, $^3J_{HH} = 8.3$ Hz and $^4J_{HH} = 1.5$ Hz); 7.49 (dd, 1H, CH arom, $^3J_{HH} = 8.3$ Hz and $^3J_{HH} = 7.2$ Hz); 7.44 (dd, 1H, CH arom, $^3J_{HH} = 4.3$ Hz and $^3J_{HH} = 8.3$ Hz); 3.62 (s, 1H, C≡CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 151.2, 136.4, 134.6, 128.9, 125.9 and 121.6 (CH arom); 148.3, 128.1 and 122.0 (C arom quat); 83.0 and 81.2 (C≡C).

Synthesis of 8-Quinolinyl-2-pyridinyl-acetylene (1). A resealable Schlenk tube was charged with 8-quinolinyl-acetylene (0.445 g, 2.90 mmol), 2-bromo-pyridine (0.460 g, 2.90 mmol), $Pd(PPh_3)_4$ (12 mg), cuprous iodide (12 mg), diethylamine (4 mL), and DMF (100 μL). The resulting mixture was heated to 50 °C and stirred at this temperature for 2 h. The reaction mixture was quenched with aqueous sodium carbonate solution (10%, 10 mL) and extracted with methylene chloride (2 × 10 mL), and the solvent of the combined organic extract was evaporated under reduced pressure. Chromatographic purification (silica gel column, EtOAc) of the resulting residue afforded a pale brown solid (0.570 g, 85% yield). Anal. Calcd for $C_{16}H_{10}N_2$ (230.27): C, 83.46; H, 4.38; N, 12.17. Found: C, 83.78; H, 4.55; N, 12.21. ^1H NMR ($CDCl_3$): δ 9.06 (dd, 1H, CH arom, $^3J_{HH} = 5.0$ Hz and $^4J_{HH} = 1.7$ Hz); 8.67−8.64 (m, 1H, CH arom); 8.17 (dd, 1H, CH arom, $^3J_{HH} = 8.3$ Hz and $^4J_{HH} = 1.7$ Hz); 8.07 (dd, 1H, CH arom, $^3J_{HH} = 7.2$ Hz and $^4J_{HH} = 1.5$ Hz); 7.84 (dd, 1H, CH arom, $^3J_{HH} = 8.3$ Hz and $^4J_{HH} = 1.2$ Hz); 7.71−7.68 (m, 2H, CH arom); 7.53 (dd, 1H, CH arom, $^3J_{HH} = 8.3$ Hz and $^3J_{HH} = 7.2$ Hz); 7.46 (dd, 1H, CH arom, $^3J_{HH} = 8.3$ Hz and $^3J_{HH} = 5.0$ Hz); 7.29−7.22 (m, 1H, CH arom). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 151.1, 149.9, 136.5, 136.0, 134.6, 129.1, 127.4, 126.0, 122.8 and 121.7 (CH arom); 148.1, 143.4, 128.2 and 122.2 (C arom quat); 94.2 and 87.0 (C≡C).

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Synthesis of Palladacycle 2. A Li_2PdCl_4 solution was prepared by dissolving $PdCl_2$ (0.186 g, 1.05 mmol) and LiCl (0.106 g, 2.50 mmol) in methanol (7 mL) with gentle heating. A solution of 8-quinolinyl-2-pyridinyl-acetylene (0.235 g, 1.02 mmol) in methanol (8 mL) was then added to the former at 0 °C. The resulting yellow suspension was stirred for 1.5 h at room temperature. The volatiles were removed under reduced pressure, the residue was taken up in a minimum amount of CH_2Cl_2, and the resulting solution was filtered through a pad of Celite. Precipitation with hexanes afforded the desired compound as a yellow solid (0.267 g, 63% yield). Anal. Calcd for $C_{16}H_{10}Cl_2N_2Pd{\cdot}1/3(CH_3)_2CO$: C, 47.82; H, 2.83; N, 6.56. Found: C, 47.62; H, 2.78; N, 6.18. IR (KBr, cm^{-1}): 1595 ($\nu_{C=C}$). ^1H NMR ($CDCl_3$): δ 9.35 (dd, 1H, CH arom, $^3J_{HH} = 4.8$ Hz and $^4J_{HH} = 1.2$ Hz); 8.98 (ddd, 1H, CH arom, $^3J_{HH} = 5.4$ Hz, $^4J_{HH} = 1.5$ Hz and $^5J_{HH} = 0.6$ Hz); 8.70 (dd, 1H, CH arom, $^3J_{HH} = 7.8$ Hz and $^4J_{HH} = 1.5$ Hz); 8.30 (dd, 1H, CH arom, $^3J_{HH} = 7.8$ Hz and $^4J_{HH} = 1.5$ Hz); 7.76 (apparent dt, 1H, CH arom, $^3J_{HH} = 7.8$ Hz and $^4J_{HH} = 1.5$ Hz); 7.77 (dd, 1H, CH arom, $^3J_{HH} = 8.1$ Hz and $^4J_{HH} = 1.2$ Hz); 7.58 (apparent t, 1H, CH arom, $^3J_{HH} = 7.8$ Hz); 7.45 (dd, 1H, CH arom, $^3J_{HH} = 8.1$ Hz and $^3J_{HH} = 4.8$ Hz); 7.45 (ddd, 1H, CH arom, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.5$ Hz, and $^5J_{HH} = 0.6$ Hz); 7.17 (ddd, 1H, CH arom, $^3J_{HH} = 7.8$ Hz, $^3J_{HH} = 5.4$ Hz, and $^4J_{HH} = 1.5$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 152.3, 151.5, 139.5, 138.3, 128.9, 128.6, 128.3, 122.6, 122.4 and 120.7 (CH arom); 165.84, 165.78, 156.0, 139.8, 129.8 and 118.4 (C arom quat and C═C).

Synthesis of Phenyl-8-quinolinyl-acetylene (4). A resealable Schlenk tube was charged with 8-quinolinyl-acetylene (0.230 g, 1.50 mmol), iodobenzene (0.408 g, 2.00 mmol), $Pd(PPh_3)_4$ (8 mg), cuprous iodide (8 mg), diethylamine (4 mL), and DMF (100 μL). The resulting mixture was heated to 50 °C and stirred at this temperature for 1 h. The reaction mixture was quenched with aqueous sodium carbonate solution (10%, 10 mL) and extracted with ether (2 × 20 mL), and the solvent of the combined organic extract was evaporated under reduced pressure. Chromatographic purification (silica gel column, hexanes/EtOAc: 90/10) of the resulting residue afforded a pale yellow liquid (0.290 g, 84% yield). CG-MS (*m*/*z*, int rel, peak): 229, 100, $M^{+\bullet}$; 202, 10, $[M - HCN]^{+\bullet}$.^1H NMR ($CDCl_3$): δ 9.08 (dd, 1H, CH arom, $^3J_{HH} = 4.2$ Hz and $^4J_{HH} = 1.9$ Hz); 8.18 (dd, 1H, CH arom, $^3J_{HH} = 8.2$ Hz and $^4J_{HH} = 1.9$ Hz); 8.03 (dd, 1H, CH arom., $^3J_{HH} = 8.0$ Hz and $^4J_{HH} = 1.4$ Hz); 7.82 (dd, 1H, CH arom, $^3J_{HH} = 8.0$ Hz and $^4J_{HH} = 1.4$ Hz); 7.76−7.70 (m, 2H, CH arom); 7.55 (apparent t, 1H, CH arom, $^3J_{HH} = 8.0$ Hz); 7.47 (dd, 1H, CH arom, $^3J_{HH} = 8.2$ Hz and $^3J_{HH} = 4.2$ Hz); 7.43−7.36 (m, 3H, CH arom). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 151.4, 136.8, 134.4, 132.3, 128.7, 128.5, 126.4 and 121.9 (CH arom); 148.3, 128.5, 123.7 and 123.6 (C arom quat); 95.7 and 87.5 (C≡C).

Attempted Chloropalladation of 4. A solution of acetylene **4** (0.162 g, 0.7 mmol) in methanol (15 mL) was added, at room temperature, to a preformed solution of Li_2PdCl_4 (0.125 g (0.7 mmol) of $PdCl_2$ and 0.075 g (1.8 mmol) of LiCl in methanol (30 mL)). The reaction mixture turns to dark brown almost instantaneously with the formation of a suspension. After 2 h of stirring at room temperature a brown precipitate was formed that was recovered by filtration, washed with methanol (2 × 15 mL), and dried under reduced pressure (165 mg). ^1H and ^{13}C NMR spectra showed that this solid is constituted of a complex mixture of products, and attempts to purify it by column chromatography or recrystallization were unsuccessful.

Synthesis of Palladacycle 6. A solution of phenyl-2-pyridinyl-acetylene (**5**) (0.304 g; 1.7 mmol) in methanol (10 mL) was added dropwise to a brown solution of Li_2PdCl_4 (0.5 g; 1,7 mmol) in methanol (50 mL) at room temperature. The orange precipitate formed after 22 h stirring at room temperature was isolated by filtration, and purification by column chromatography on silica (CH_2Cl_2) affords a yellow solution. Concentration of this solution to 3−5 mL and addition of hexane (20 mL) affords a yellow solid that has been recovered by filtration washed with hexane (3 × 15 mL) and dried under reduced pressure (0.426 g, 70% yield). Mp: 148−150 °C (decomposition). Anal. Calcd for $C_{13}H_9Cl_2NPd$: C, 43.80; H, 2.52; N, 3.93. Found: C, 43.50; H, 280; N, 3.70. IR (KBr, cm^{-1}): 1579 ($\nu_{C=N}$). ^1H NMR ($CDCl_3 + \epsilon$Py-d_5)): δ 8.85 (m, 1H, o-Py, $^3J_{HH}$= 5.6 Hz); 7.81 and 7.37 (2m, 8H, aromatic). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 178.1 and 120.2 (C═C); 163.7, 149.4, 139.7, 128.1, 127.4, 125.8, 121.9 (CH aromatic), 142.7, 118.2 (C quat aromatic).

Computational Details. The density functional theory calculations were performed at the B3LYP level[11] using the Gaussian 98 program package.[12] The basis set for the palladium and chloro atoms were the LANL2DZ with the corresponding effective core potential,[13] and the DZ Dunning-Hay basis set complemented with polarization and diffuse functions (with the exception of the hydrogen atoms)[14] was used for the remaining atoms. Initially, a completely optimized geometry was obtained and an excitation energies calculation was performed using the time dependent theory (TD-DFT).[15]

Quantum Yield of Fluorescence. For quantum yield of fluorescence, a Shimadzu UV-1601PC spectrophotometer and a Hitachi spectrofluorometer model F-4500 were applied. The quantum yield of fluorescence (ϕ_{fl}) was determined at 25 °C in spectroscopic grade ethanol solution (Merck). Quinine sulfate (Riedel) in H_2SO_4 1 M ($\phi_{fl} = 0.55$)[16] was used as quantum yield standard.

Laser Flash Photolysis. The laser flash photolysis experiments were carried out with an Edinburgh Analytical Instruments LP900 laser flash photolysis system equipped with a Surelite I-10 Nd: YAG laser for excitation and a 450 W high-pressure xenon lamp for monitoring transient absorption. A solution of the Pd complex in acetonitrile (with an absorbance of ca. 0.5 at 355 nm), contained in standard 1 cm path length quartz fluorescence cuvette, was excited with the third harmonic (5 ns halfwidth pulses at 355 nm)

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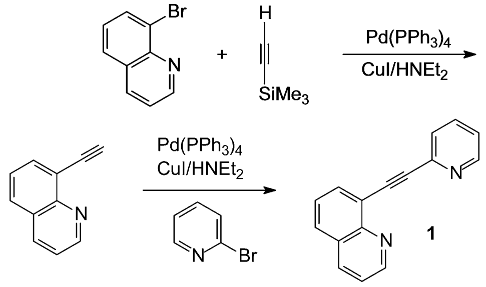
Scheme 1. Preparation of Alkyne **1** from 8-Bromoquinoline

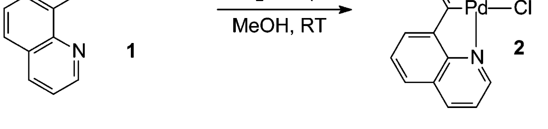


of the Nd:YAG laser. Solutions were stirred between each laser shot, and 5 laser shots were averaged to obtain the transient absorption decays. Lifetime measurements were performed at 20 °C on air-equilibrated solutions and on solutions deoxygenated by exhaustive purging with argon in cuvettes capped with a rubber septum. Solutions were monitored for laser-induced decomposition by conventional UV−vis absorption spectroscopy (Hewlett-Packard 8452A diode array spectrometer) and replaced by fresh solution at the first signs of decomposition. The standard exponential decay routines of the Edinburgh Analytical Instruments LP900 system software were used to analyze the decays of the transient and obtain the lifetimes of the excited species. In all cases, a single exponential adequately described the decay. Transient absorption spectra were determined point-by-point, and in all cases, the lifetime of the transient showed no significant variation with wavelength.

Results and Discussion

Preparation of the Ligand and Chloropalladation. Initial attempts to prepare 2-pyridinyl-8-quinolinyl-acetylene **1** by Sonogashira[17] coupling of the commercially available 2-pyridinyl-acetylene with 8-bromoquinoline under various reaction conditions failed. However, the alkyne **1** was easily prepared in two steps starting from 8-bromoquinoline as presented in Scheme 1. Alkyne **1** was isolated in 65% overall yield as a white powder and characterized by means of CHN combustion analysis, CG-MS, IR, UV−vis, and ^{1}H and ^{13}C NMR (see Experimental Section).

The addition of alkyne **1** to a methanolic solution of Li_2PdCl_4 at room temperature affords almost instantaneously and in high yields the pincer palladacycle **2** (eq 1). Palladacycle **2** was isolated as a yellow crystalline solid and is air and water stable, soluble in most of polar organic solvents (dichloromethane, acetone, toluene, etc.), and insoluble in nonpolar solvents such as hexane and diethyl ether. Compound **2** has a relatively high thermal stability since it only starts to decompose at temperatures above 140 °C.



(1)

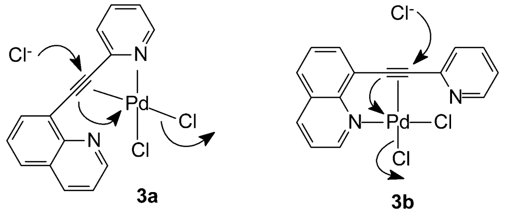


Figure 2. Postulated intermediates in the chloropalladation of **1**.

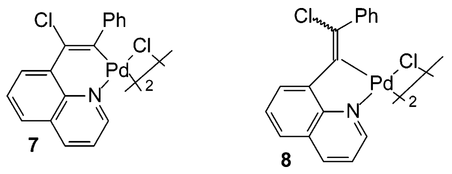
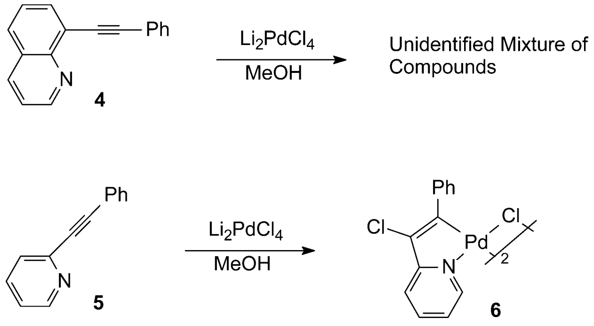


Figure 3. Possible palladacycles produced by the chloropalladation of **4**.

Scheme 2



The formation of **2** probably occurs through the coordination of only one donor group followed by coordination of the C≡C triple bond yielding intermediates such as **3** (Figure 2). Selective intermolecular chloride nucleophilic addition on the activated C≡C bond affords the more thermodynamic stable five-membered palladacyclic ring followed by coordination of the second donor group affording **2**.

Modeling experiments suggest that the simultaneous coordination of the quinoline nitrogen and the alkyne to the Pd center to generate an intermediate like **3b** is more favorable than the formation of **3a**. However, evidence suggesting the preferential coordination of the pyridine moiety rather than N-quinoline atom and formation of the five-membered ring have been obtained from the reactions of phenyl-8-quinolinyl-acetylene (**4**) and phenyl-2-pyridinyl-acetylene (**5**) with Li_2PdCl_4 (Scheme 2).

The reaction of phenyl-8-quinolinyl-acetylene (**4**) affords a mixture of unidentified compounds together with $PdCl_2$ and metallic palladium whereas the same reaction using phenyl-2-pyridinyl-acetylene (**5**) affords the chloro dimer palladacycle **6**. In the case of **4**, the chloropalladation can generate a six-membered ring palladacycle **7** or a five-membered ring containing an exo-cyclic double bond **8** (Figure 3) depending on the regiochemistry of chloride nucleophilic addition. These types of dimeric compounds are apparently not stable since previous attempts using analogous alkynes (possessing the homo propargyl skeleton) have failed.[7] In contrast the formation of five-membered palladacycles containing the endocyclic double like in **6** is a general case for the chloropalladation of heterosubstituted alkynes.[7]

Crystal Structure of 2. The molecular structure of **2** has been ascertained by means of an X-ray diffraction analysis.

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(17) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467−4470.

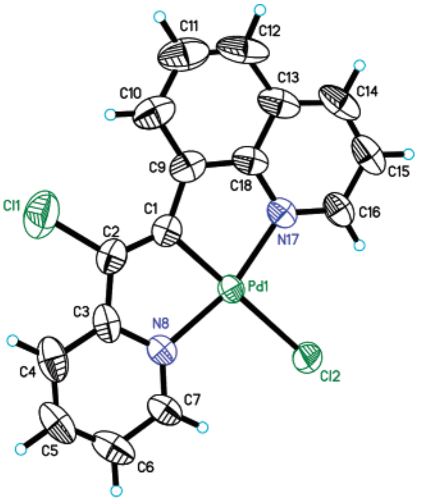

Figure 4. Molecular structure of the complex (C_5H_4N-2-C=C(Cl)-8-$C_9H_6\kappa N,\kappa C,\kappa N$)PdCl (**2**). Selected bond lengths (Å) and angles (deg): Pd1−C1 1.955(5), Pd1−N17 2.035(4), Pd1−N8 2.040(4), Pd1−Cl2 2.407(14), C1−Pd1−N17 82.7(2), C1−Pd1−N8 82.13(19), N17−Pd1−N8 164.85(17), C1−Pd1−Cl2 178.64(15), N17−Pd1−Cl2 96.93(13), C7−N8−Pd1 127.5(4), C3−N8−Pd1 112.6(3), C16−N17−Pd1 127.4(4), C18−N17−Pd1 112.5(3).

Table 1. Summary of the Crystal Data and Structure Refinement for **2**

empirical formula	$C_{15}H_{11}Cl_3N_2Pd$
fw	450.02
temp	200(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	*C*2/*c*
Z	8
unit cell dimensions	$a = 17.6947(4)$ Å, $\alpha = 90°$ $b = 7.8438(2)$ Å, $\beta = 92.881(1)°$ $c = 23.1986(5)$ Å, $\gamma = 90°$
V	3215.75(13) Å^3
D(calcd)	1.86 g/cm^3
abs coeff	1.65 mm^{-1}
cryst shape	needle
cryst size	$0.47 \times 0.06 \times 0.02$ mm^3
θ range for data collection	1.8−24.1°
index ranges	$-20 \leq h \leq 20$ $-9 \leq k \leq 9$ $-26 \leq l \leq 26$
reflns collected	12149
indep reflns	2541 (R(int) = 0.0602)
obsd reflns	1894 ($I > 2\sigma(I)$)
abs correction	semiempirical from equivalents
max and min transm	0.98 and 0.84
refinement method	full-matrix least-squares on F^2
data/restraints/params	2541/0/204
GOF on F^2	1.01
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.037, wR2 = 0.079
largest diff peak and hole	0.70 and −0.56 e Å^{-3}

An ORTEP drawing of the structure is shown in Figure 4 together with selected bond distances and angles. Crystallographic data and details of the structure determination are presented in Table 1. Tables of atomic coordinates, hydrogen coordinates, complete list of bond distances and angles, and anisotropic thermal parameters are supplied as Supporting Information.

In compound **2**, the Pd(II) center is coordinated in a slightly distorted square-planar fashion by the pyridine N donor groups, a C(sp^2) vinyl atom of the anionic terdentate ligand system, and a Cl atom. The C(vinyl)−Pd−Cl bond angle is 179°, and the two N donor groups are also in mutual *trans* positions with a bond angle of 165° showing an angular deviation of 15° from an exact *trans* coordination. This distortion from the ideal square-planar arrangement is the result of the small C(1)−Pd(1)−N(17) and C(1)−Pd(1)−N(8) bite angles in the two five-membered rings, of 83° and 82°, respectively. The σ Pd−C(vinyl) single bond length in **2** of 1.95 Å is of the same order of magnitude of those observed in similar compounds, where the distances fall in the range between 1.991 and 2.011 Å.[18] The two five-membered rings are almost perfectly flat.

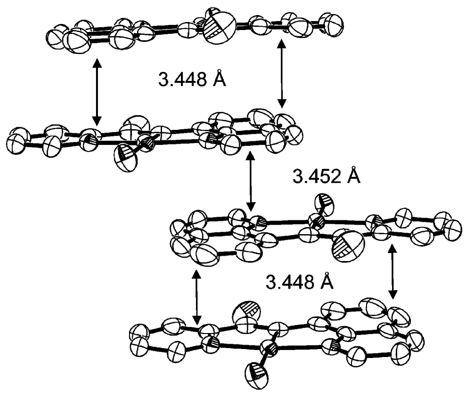

Figure 5. Diagram showing the $\pi-\pi$ stacking arrangement (pyridine−quinoline and quinoline−quinoline interactions) along the *b* axis.

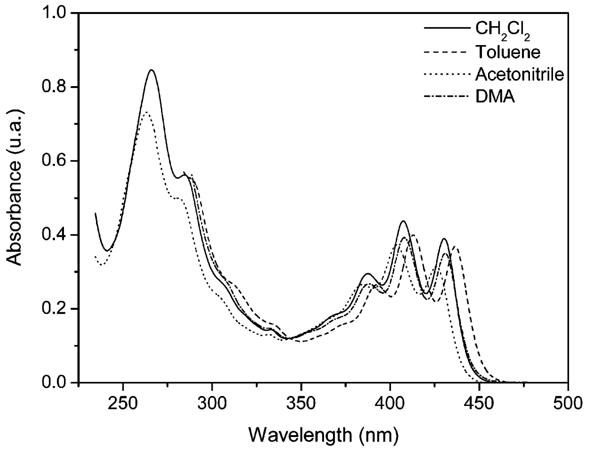

Figure 6. UV−vis absorption spectra of **2**.

The crystal structure packing of **2** consists of inversion related pairs of molecules through aromatic $\pi-\pi$ stacking (Figure 5). The pairs are arranged in a head-to-tail manner and involve the close interaction of pyridine and quinoline moieties (3.448 Å) and a large Pd−Pd distance (5.004 Å). The stacking along the *b* axis through quinoline−quinoline interactions is 3.452 Å.

UV−Vis Characterization and Theoretical Calculations. The UV−vis spectra of complex **2** are presented in Figure 6, and the absorption bands are summarized in Table 2.

The complex has intense absorption bands at 263 nm (CH_2Cl_2) and 266 nm (CH_3CN) that are probably related to the ligand-centered transition ($\pi-\pi^*$). Moderate absorptions were also observed between 385 and 437 nm with molar

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(18) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Robin Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1−S83.

Table 2. UV−Vis Absorption Data **2**[a]

solvent	λ_{max}^{abs} (nm)
dichloromethane	266 (2.9), 388 (1.0), 408m (1.5), 431 (1.3)
toluene	393 (0.8), 413m (1.3), 437 (1.2)
acetonitrile	263 (2.5), 385 (0.9), 404m (1.2), 426 (1.1)
DMA	389 (0.9), 409m (1.4), 432 (1.2)

[a] In parenthesis are presented the molar extinction coefficients values ($\epsilon_{max} = \times 10^{-4}$ L·mol^{-1}·cm^{-1}).

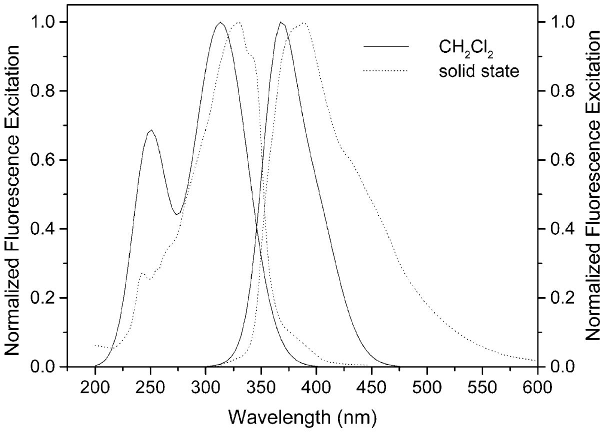

Figure 7. Normalized solid state and CH$_2$Cl$_2$ solution (10^{-5} mol·L^{-1}) fluorescence spectra of the ligand **1**.

extinction coefficients in the range 0.8 × 10^4 to 1.5 × 10^4 L·mol^{-1}·cm^{-1}. It can also be seen that the solvent polarity does not present a fundamental role in the maximum absorption wavelength. However, this small solvatochromic shift is an indication of their charge-transfer nature. Of note is that the bands at 350−450 nm have been ascribed to metal-perturbed intraligand transitions for analogous cyclopalladated CN aromatic compounds.[19−21]

In order to get some insight into the nature of these transitions, we carried out molecular orbital calculations for pincer palladacycle **2** using density functional theory. The LUMO orbitals of **2** are basically π^* (LUMO; LUMO + 1, LUMO + 2, and LUMO + 3), mainly centered on the quinoline−pyridine ligand with little palladium contribution, and σ^* (LUMO + 4). The (first) HOMO and HOMO − 2 orbitals are characteristically π while the remaining first HOMOs are σ orbitals including the HOMO − 4 orbital with remarkable metal d(z^2) character. On the basis of the TD-DFT calculations, the strongest transitions can be attributed, considering the main contribution, to HOMO − 2 → LUMO (393.2 nm, oscillator strength (os) 0.19), HOMO → LUMO + 1 (409.4 nm, os 0.02), and HOMO → LUMO (480.8 nm, os 0.07) transitions with $\pi \rightarrow \pi^*$ character.

Fluorescence Characterization. The 2-pyridinyl-8-quinolinyl-acetylene **1** is an emitter in both solution and in the solid state with emission maxima of 389 nm (Figure 7).

The Pd complex is also fluorescent in solution and in the solid state when irradiated with UV light at room temperature. The λ_{max}^{abs} obtained by UV−vis spectra were used as excitation wavelengths for fluorescence emission spectra. The Pd complex fluorescence spectra are presented in Figure 8. Relevant data obtained by fluorescence are listed in Table 3.

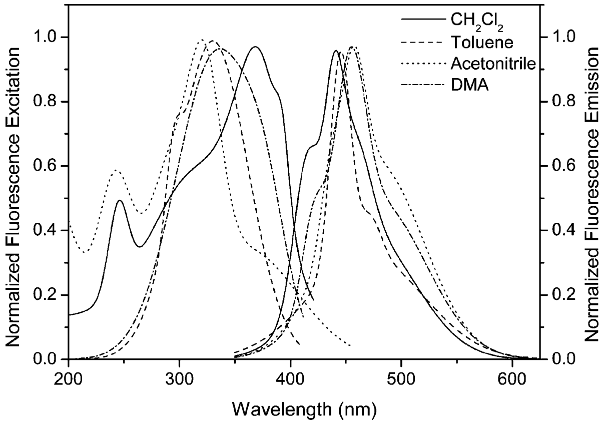

Figure 8. Normalized steady-state fluorescence spectra of the Pd complex.

Table 3. Fluorescence Data of **2** in Solution

solvent	λ_{max} excitation (nm)	λ_{max} emission (nm)	Stokes shift (nm)
CH$_2$Cl$_2$	369	442	73
toluene	331	447	116
acetonitrile	320	457	137
DMA	338	457	118

Values of maximum excitation fluorescence between 320 and 369 nm could be detected for the Pd complex. The complex presented emission spectra in the blue region with a maximum emission wavelength range of 442−457 nm. As it can be seen, the solvent polarities affect the maximum emission of fluorescence. The local environment can affect the energies of both the ground and excited states. Polar solvents can stabilize all electronic states, but the larger the dipolar moment of the electronic state, the greater the stabilization energy. In this way, transitions would be red-shifted in polar solvents due to the high stabilization of these orbitals, as can be detected for DMA compared with toluene and CH$_2$Cl$_2$. Using acetonitrile as a solvent, a similar value obtained with DMA could be observed. The luminescence displayed by **2** in solution at room temperature is unprecedented for mononuclear palladacycles, which usually display strong luminescence only in a rigid matrix at 77 K.[6]

Solid state fluorescence spectra of the Pd complex have also been measured at room temperature and can be seen in Figure 9. A single emission (501 nm) and excitation (322 nm) band could be seen for the complex with a Stokes shift of 179 nm. This value in the solid state is higher than those obtained in solution, indicating that the solvent plays a fundamental role in the complex fluorescence emission mechanism. Moreover, the different values (red-shifted) obtained for the emission in solution and solid state suggest that emission in the solid state can be attributable to excimeric species. The excimeric emission can result from metal−metal to ligand charge transfer (MMLCT) where the donor orbital is derived from the metal−metal interaction or $\pi-\pi^*$ emission resulting from the aromatic stacking interactions between the metalated ligands.[6] It is, however,

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(19) Ghedini, M.; Pucci, D.; Calogero, G.; Barigelletti, F. *Chem. Phys. Lett.* **1997**, *267*, 341−344.

(20) Aiello, I.; Ghedini, M.; La Deda, M. *J. Lumin.* **2002**, *96*, 249−259.

(21) Fernández, S.; Forniés, J.; Gil, B.; Gómez, J.; Lalinde, E. *J. Chem. Soc., Dalton Trans.* **2003**, 822−830.

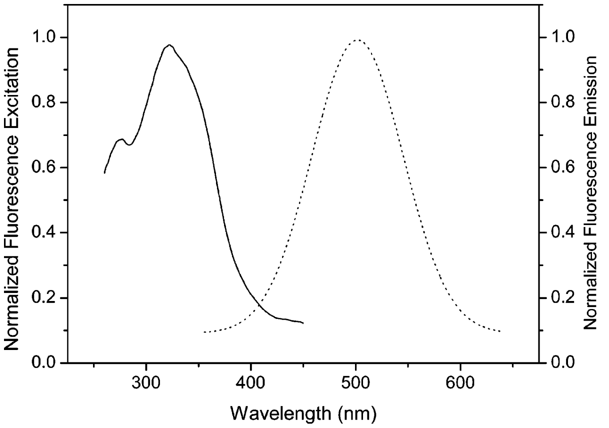

Figure 9. Normalized solid state fluorescence spectra of the Pd complex **2**.

very difficult to unambiguously assign the contribution of one of these interactions. In the case of **2**, the long Pd−Pd distance (5.004 Å) compared with other similar palladacycles (3.27 Å observed in 6-phenyl-2,2′-bipyridine, for example)[6] and the relatively short π-stacking (quinoline−quinoline interactions = 3.452 Å, see Figure 5) suggests that excimeric $\pi-\pi^*$ may be responsible for the observed transition in the solid state.

Palladacycle **2** is a very weak fluorescent emitter, and the quantum yield of fluorescence for complex **2** (6.8×10^{-3}) is lower than of the ligand **1** (3.0×10^{-2}), both relative to quinine sulfate ($\phi_{\mathrm{fl}} = 0.55$). Our assignment of the weak emission of the Pd complex as being fluorescence rather than room-temperature phosphorescence is confirmed by laser flash photolysis experiments on the Pd complex in acetonitrile solution. Upon excitation of the complex at 355 nm (Nd:YAG laser, 5 ns pulse), a single transient was observed. The transient absorbs across the entire visible spectral range (400−800 nm) and decays exclusively back to ground state; thus, the lifetime determined from decay of the transient (e.g., at 550 nm) is identical to that obtained by monitoring the recovery of the ground-state absorption at 410 nm, and no longer-lived species are observed. In air-equilibrated acetonitrile, the decay of the transient is monoexponential at all wavelengths monitored (400−800 nm), with a lifetime of 197 ± 5 ns. Upon purging the solution with argon to remove oxygen, the lifetime of the transient increases to 2.0 ± 0.1 μs, indicating that it is the triplet state of the Pd complex. In contrast, the intensity of the emission of the complex is only marginally enhanced (by only a few percent) upon argon purging of the solution, confirming that the observed emission is inefficiently quenched by oxygen and is therefore fluorescence rather than phosphorescence.

In summary, we have shown that chloropalladation is a simple and useful method for the construction of rigid and totally flat pincer palladacycles that display luminescence properties. The palladacycle **2** exhibits fluorescence at room temperature in both the solid state and in solution. This property is probably a result of excimeric transitions due to the particular structure of this compound (rigid and totally flat).

Acknowledgment. Financial support from FAPERGS, and CNPq (Brazil), is gratefully acknowledged. Thanks are also due to FAPESP and CAPES for fellowships.

Supporting Information Available: Tables of full crystal data, atomic coordinates, calculated hydrogen coordinates, anisotropic thermal parameters; a complete list of bond lengths and angles; and Gaussian98 output files containing full optimized geometry and excited state energy calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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