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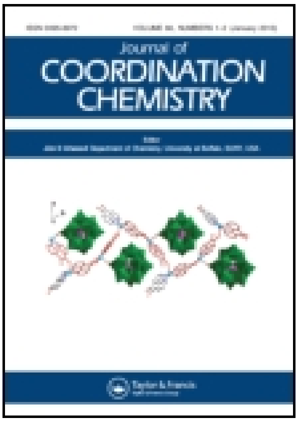

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# Synthesis, structure, and spectroscopy of two benzil-based α-diimine ligands and their palladium(II) complexes

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Two α-diimine ligands were prepared in 60–70% yield via *p*-toluenesulfonic acid-catalyzed condensation reactions from benzil with 4-bromoaniline and with *p*-anisidine. Palladium(II) complexes were prepared from both ligands in 70–80% yield. X-ray structures were obtained for the ligand prepared from *p*-anisidine and its palladium(II) complex. A notable feature observed in the former was its unconjugated C–N double bonds, both in the (*E*)-configuration. The latter structure possessed two molecules of the metal complex in its unit cell, both of which have diimine cores with a degree of conjugation and a nonideal square-planar geometry around palladium caused by the small bite angles (79.61(3) and 79.15(3)°) of the diimine ligands. Solution-phase electronic absorption spectra of the ligands in chloroform have two bands from $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions at 269–345 nm. Absorption spectra of the complexes in chloroform exhibited bands attributed to ligand-centered transitions that were red-shifted as compared to free ligands. Only the spectrum obtained from a chloroform solution of the palladium(II) complex with the diimine ligand prepared from *p*-anisidine featured a band at approximately 520 nm, which was assigned to a combination of $d_\pi(\text{Pd}) \rightarrow \pi^*$ and $n(\text{Cl}) \rightarrow \pi^*$ transitions.

*Keywords*: Benzil-based α-diimine ligands; Palladium(II) complexes; X-ray crystal structure; Electronic absorption spectra

## 1. Introduction

α-Diimines (RN=C(R′)–C(R′)=NR) are a versatile and popular class of Schiff base. This popularity arises from ease of preparation, which permits tremendous leeway in tuning of steric and electronic properties [1, 2], in contrast to phosphines, another popular class of ligands, whose syntheses are generally more challenging [3].

Many different research areas utilize α-diimines, as bidentate ligands capable of binding to a variety of transition metals, but even on their own they are quite useful. For example, free α-diimines have been used as precursors to heterocyclic compounds as well as molecules with unique π-architectures [4, 5]. α-Diimines have also been used to prepare other ligands, such as annulated N-heterocyclic carbenes [6]. Rhenium(I) tricarbonylchloro

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*Corresponding author. Email: risovits@whittier.edu complexes possessing α-diimine ligands constructed upon an acenaphthene scaffold were examined as photosensitizers in photovoltaic devices [7]. α-Diimine ligands have been extensively used to prepare palladium(II) complexes as catalysts for the polymerization of α-olefins.

Seminal work in this area was done by Brookhart and coworkers with their discovery that palladium(II) complexes with bulky α-diimine ligands possessing methyl, isopropyl, and acenaphthene moieties catalyzed the polymerization of ethene, propene, and 1-hexene [8]. Since this discovery, numerous palladium(II) complexes with α-diimine ligands have been prepared and the mechanism of how they effect the polymerization of α-olefins explored [9–12].

The steric and electronic properties of palladium(II) α-diimine polymerization catalysts have been altered toward the goals of controlling the characteristics of the polymers they produce and their overall efficacy. One recent study that probed ligand electronic effects on these catalysts discovered that electron-donating and electron-withdrawing groups in the *para* position on the phenyl rings of the α-diimine affected the molecular weight and topology of the polymer produced [13]. Alteration of the functionality of the imine carbons of an α-diimine has also been used as a strategy for tailoring electronic properties of polymerization catalysts that are prepared from them. For example, α-diimine ligands substituted with electron-perturbing chloro or fluorenyl groups on each of their imine carbons have been used to prepare palladium(II) complexes [14]. The effect of sterics on polymer production has been examined via catalysts that possess α-diimine ligands with bulky moieties, such as substituted 2,6-diphenylanilines and cyclophanes [12, 15].

Our research explores the preparation of α-diimines and their metal complexes with the goal of applying them to catalysis of C–C bond forming reactions, such as the Heck reaction. In this article, we report the synthesis of two α-diimine ligands based on benzil and their palladium(II) complexes. The X-ray structures of one of our ligands and its palladium(II) complex are also presented. The electronic absorption spectra of the ligands and their palladium(II) complexes are also compared.

## 2. Experimental

### 2.1. *Materials and physical measurements*

Synthetic procedures were carried out using standard techniques. Solvents and reagents were purchased from Sigma–Aldrich or Acros Organics and used as received. Melting points were determined in open capillaries and are uncorrected. $^1$H and $^{13}$C NMR spectra were recorded on a JEOL ECX 300 MHz spectrometer using TMS as the internal standard. IR spectra were recorded neat or as KBr and KCl disks on a Perkin–Elmer Spectrum 1 FT-IR. Elemental analyses were done by M-H-W Laboratories of Tucson, Arizona. Mass spectrometry for **1** and **3** was provided by the Washington University Mass Spectrometry Resource with support from the NIH National Center for Research Resources (Grant No. P41RR0954).

Electronic absorption spectra were recorded from solutions prepared from spectrophotometric grade chloroform, utilizing a Hewlett Packard 8453 diode array spectrometer. All solutions were approximately 2–4 × $10^{-5}$ M.

### 2.2. *Preparation of the α-diimine ligands and their palladium(II) complexes*

**2.2.1. Preparation of *N,N′*-di(4-bromophenyl)-1,2-diphenylethane-1,2-diimine (1).** A 50 mL round-bottom flask was charged with benzil (0.603 g, 2.87 mmol, 1 eq), 4-bromoaniline (2.11 g, 12.28 mmol, 4.3 eq), *p*-toluenesulfonic acid (0.274 g, 1.44 mmol, 0.5 eq), and a magnetic stirbar. Methanol (10 mL) was added to the round-bottom flask and the reaction mixture refluxed overnight. The reaction mixture was cooled and the resulting yellow precipitate was collected via vacuum filtration and washed with room temperature water. After drying, 1.04 g (70%) of a light yellow solid was obtained. m.p. 204–206 °C. IR (KBr) 3031, 1610, 1594, 1577 cm$^{-1}$. $^1$H NMR (300 MHz, DMSO-d$_6$) δ 7.76 (d, $^3J = 7.6$ Hz, 4 H), 7.45 (m, 6 H), 7.32 (d, $^3J = 8.6$ Hz, 4 H), 6.40 (d, $^3J = 8.3$ Hz, 4 H). $^{13}$C NMR (75 MHz, DMSO-d$_6$) δ 164.5, 148.4, 136.8, 132.5, 132.1, 129.7, 128.6, 122.2, 118.1. Anal. Calcd for $C_{26}H_{18}N_2Br_2$ (%): C, 60.25; H, 3.50; N, 5.41. Found: C, 60.34; H, 3.72; N, 5.39. HR-ESI-MS: 516.9923 ([M+H]$^+$; calcd 516.9915).

**2.2.2. Preparation of *N,N′*-di(4-methoxyphenyl)-1,2-diphenylethane-1,2-diimine (2).** A similar procedure as **1** using benzil (0.684 g, 3.25 mmol, 1 eq), *p*-anisidine (2.10 g, 17.08 mmol, 5.3 eq) and *p*-toluenesulfonic acid (0.301 g, 1.58 mmol, 0.5 eq) gave **2**, except using a small amount of cold methanol as a washing solvent. After drying, 0.832 g (60%) of a canary yellow solid was obtained. m.p. 167–169 °C. IR (KBr) 3034, 2950, 1612, 1575, 1242 cm$^{-1}$. $^1$H NMR (300 MHz, $CD_2Cl_2$) δ 7.83 (m, 4 H), 7.38 (m, 6 H), 6.65 (m, 8 H), 3.69 (s, 6 H). $^{13}$C NMR (75 MHz, $CD_2Cl_2$) δ 163.1, 157.5, 142.4, 137.3, 130.9, 128.7, 128.0, 122.2, 113.7, 55.3. Anal. Calcd for $C_{28}H_{24}N_2O_2$ (%): C, 79.97; H, 5.75; N, 6.66. Found: C, 79.73; H, 5.63; N, 6.61. HR-ESI-MS: 421.1917 ([M + H]$^+$; calcd 421.1916).

**2.2.3. Preparation of dichloro[*N,N′*-di(4-bromophenyl)-1,2-diphenylethane-1,2-diimine]palladium(II) (3).** 0.100 g (0.192 mmol, 1 eq) of **1**, 0.099 g (0.297 mmol, 1.5 eq) of Pd$(DMSO)_2Cl_2$, and 8 mL of methanol were added to a 50 mL round-bottom flask and the reaction mixture was refluxed. After 30 min, a dark orange precipitate formed was collected via vacuum filtration and air-dried, giving 0.115 g (86%) of pure **3**. m.p. > 250 °C. IR (KCl) 3057, 1480, 1384 cm$^{-1}$. Anal. Calcd for $C_{26}H_{18}N_2Cl_2Br_2Pd$ (%): C, 44.89; H, 2.61; N, 4.03. Found: C, 45.08; H, 2.81; N, 4.00. HR-ESI-MS: 718.8127 ([M + Na]$^+$; calcd 718.8121).

**2.2.4. Preparation of dichloro[*N,N′*-di(4-methoxyphenyl)-1,2-diphenylethane-1,2-diimine]palladium(II) (4).** 0.126 g (0.299 mmol, 1 eq) of **2**, 0.100 g (0.299 mmol, 1 eq) of Pd$(DMSO)_2Cl_2$, and 10 mL of methanol were added to a 50 mL round-bottom flask and the reaction mixture stirred at room temperature. After stirring for 30 min, a red-orange precipitate formed. The precipitate was collected via vacuum filtration and air-dried. The precipitate was dissolved in a minimum of $CH_2Cl_2$ and the resulting red solution placed in a test tube and layered with an equal volume of cyclohexane [16]. The test tube was then tightly stoppered and left undisturbed. After two days, red needles of **4** formed, were collected using vacuum filtration and air-dried, giving 0.097 g (77%) of pure **4**. m.p. > 250 °C.

IR (KCl) 3057, 2930, 1601, 1503, 1444, 1249 $cm^{-1}$. $^1H$ NMR (300 MHz, $CD_2Cl_2$) δ 7.03 (m, 10 H), 6.81 (d, $^3J = 7.2$ Hz, 4 H), 6.67 (d, $^3J = 8.9$ Hz, 4 H), 3.71 (s, 6 H). $^{13}C$ NMR (75 MHz, $CD_2Cl_2$) δ 178.2, 158.9, 139.1, 132.5, 130.0, 128.5, 128.2, 125.9, 112.8, 55.4. HR-ESI-MS: 621.0121 ($[M+Na]^+$; calcd 621.0142).

### 2.3. *X-ray structure determination of 2 and 4*

X-ray quality crystals of **2** and **4** were used for data collection at T = 90 K. The data for **2** were collected on a Bruker Kappa APEX-II CCD diffractometer equipped with an Oxford Cryosystems Cryostream chiller and graphite-monochromated Cu *K*α radiation (λ = 1.54178 Å). The data for **4** were collected on a Bruker Kappa APEX-II DUO diffractometer equipped with an Oxford Cryosystems Cryostream chiller and graphite-monochromated Mo *K*α radiation (λ = 0.71073 Å). The crystal of **4** was kept wet with its crystallizing solvents prior to structure determination. Structures were solved by direct methods, and structure refinements were carried out using SHELXL-97 [17]. All hydrogens were visible in difference maps, but were placed in idealized positions during refinement with a torsional parameter refined for the methyl groups.

CCDC 884,594 and 884,595 contain the Supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/products/csd/request/ (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336,003).

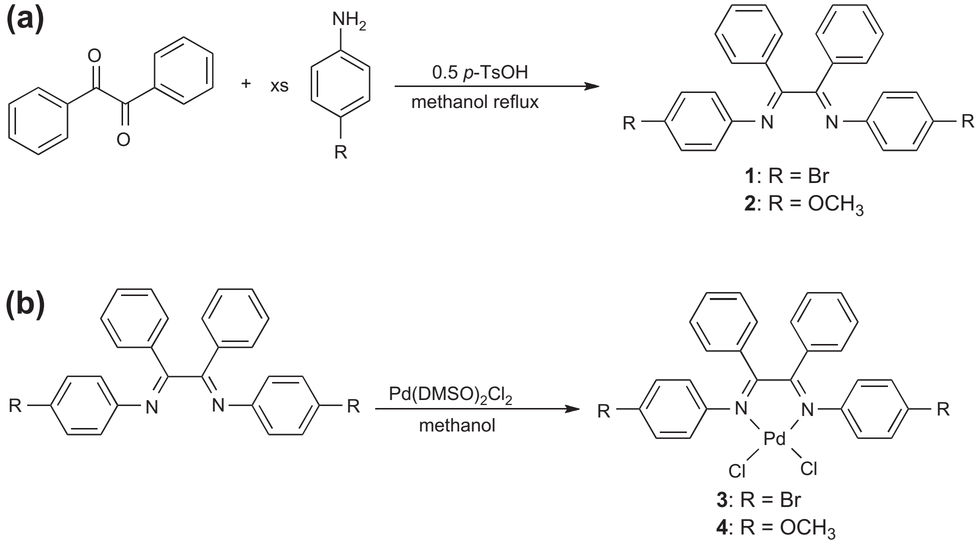
## 3. Results and discussion

### 3.1. *Synthesis and characterization of 1–4*

Condensation reactions are the typical route to α-diimines [18]. Compounds **1** and **2** were obtained analytically pure in 60–70% yield from *p*-toluenesulfonic acid-catalyzed condensation between benzil and the corresponding aniline derivative (Scheme 1) [1]. Compound **1** exhibited spectroscopic characteristics that indicated product formation, for example, a peak at 164.5 ppm in the $^{13}C$ NMR spectrum that was assigned to the imine carbon [19]. Spectra of **2** compared well with those found in the literature [20]. Both **1** and **2** had HR-ESI-MS that exhibited $[M+H]^+$ peaks at $m/z = 516.9923$ and 421.1917, respectively. These values both varied no more than 3 ppm from the calculated values. The identity and purity of **1** and **2** were supported by acceptable elemental analyses.

Reactions of $Pd(DMSO)_2Cl_2$ with **1** and **2** in methanol (the former at room temperature and the latter under reflux) resulted in formation of the corresponding palladium(II) complexes, **3** and **4**, in 70–80% yield [21, 22]. Compound **3** was isolated in pure form from the reaction mixture, while **4** was obtained in pure crystalline form by diffusing cyclohexane into a concentrated dichloromethane solution of the crude complex [16].

Different analytical techniques indicated complexation of **1** and **2**. The peaks in the $^1H$ and $^{13}C$ NMR spectra of **4** showed a general downfield shift when compared to those of its parent ligand. For example, the imine carbon resonance in the $^{13}C$ NMR spectrum shifted from 163.1 to 178.2 ppm. The IR spectrum of **3** was different from that of its precursor ligand. However, its NMR spectra in DMSO-$d_6$ solution were identical with those of the free ligand. This was attributed to DMSO-$d_6$, a complexing solvent with two



Scheme 1. (a) The synthesis of **1** and **2**. (b) The synthesis of **3** and **4**.

potential donor sites, displacing the coordinated diimine from **3** [22, 23]. α-Diimine ligands with electron-withdrawing groups, such as **1**, have been shown to have low coordination strength for palladium(II) [24]. The low solubility of **3** in noncomplexing deuterated solvents, also a trait of palladium(II) complexes that possess a diimine ligand with electron-withdrawing groups, prohibited the acquisition of useful $^{1}$H and $^{13}$C NMR spectra. The HR-ESI-MS of **3** and **4** had $[M+Na]^{+}$ peaks at $m/z = 718.8127$ and 621.0121, which varied no more than 3 ppm from the calculated values, and exhibited the predicted isotope pattern for species that contain palladium. The identity and purity of **3** were verified by elemental analysis. Four trials failed to give an acceptable elemental analysis of **4**. This was explained by its intercollated dichloromethane (which was revealed by the X-ray crystal structure), whose amount would vary due to environmental conditions, which in turn would cause inconsistent elemental composition. Representative $^{1}$H and $^{13}$C NMR spectra of **4**, with expansions of the aromatic regions of each, are provided in the Supplementary material as evidence of its homogeneity.

### 3.2. *Crystal and molecular structures*

The crystallographic data, collection parameters, and structure refinement details for **2** and **4** are presented in table 1, while selected bond lengths and angles are listed in table 2. The *ORTEP* representation of **2** is shown in figure 1 and that of **4** is shown in figure 2. The crystal packing of **2** is illustrated in figure 3, while that of **4** is shown in figure 4.

**3.2.1. Molecular structure and crystal packing of 2.** The C–N double bonds, N1–C1 and N2–C2, in **2** both adopt an (*E*)-configuration. The length of these bonds, 1.2792(15) and 1.2820(15) Å, respectively, correspond to a $C(sp^{2})$–$N(sp^{2})$ double bond in a

Table 1. Crystallographic data and collection parameters for **2** and **4**.

| Compound | **2** | **4** |
|---|---|---|
| Empirical formula | $C_{28}H_{24}N_2O_2$ | $C_{28}H_{24}Cl_2N_2O_2Pd\cdot 0.5(CH_2Cl_2)$ |
| Formula weight | 420.49 | 640.26 |
| Temperature (K) | 90 | 90 |
| Crystal system | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| Unit cell dimensions (Å, °) | | |
| $a$ | 9.3684(7) | 12.2640(5) |
| $b$ | 9.8418(8) | 15.3089(6) |
| $c$ | 13.3896(10) | 16.3839(6) |
| $\alpha$ | 76.289(3) | 68.136(2) |
| $\beta$ | 80.578(3) | 73.874(2) |
| $\gamma$ | 67.136(3) | 74.769(2) |
| Volume (Å$^3$), $Z$ | 1101.59(15), 2 | 2698.35(18), 4 |
| Calculated density (Mg m$^{-3}$) | 1.268 | 1.576 |
| Absorption coefficient (mm$^{-1}$) | 0.63 | 1.01 |
| $F(000)$ | 444 | 1292 |
| Crystal size (mm) | 0.25 × 0.21 × 0.16 | 0.34 × 0.21 × 0.09 |
| θ range for data collection (°) | 3.4–67.8 | 2.4–40.0 |
| Radiation | Cu Kα | Mo Kα |
| Reflections collected | 14,137 | 113,060 |
| Independent reflections | 3858 [$R$(int) = 0.046] | 33,140 [$R$(int) = 0.026] |
| Observed reflections, $I > 2\sigma(I)$ | 3596 | 28,367 |
| Goodness-of-fit on $F^2$ | 1.04 | 1.0 |
| $R$ indices | $R_1 = 0.037$, $wR_2 = 0.098$ | $R_1 = 0.026$, $wR_2 = 0.066$ |
| $(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ | 0.24, −0.21 e Å$^{-3}$ | 1.15, −1.23 e Å$^{-3}$ |

nonconjugated organic molecule. The lack of conjugation between the C–N double bonds was supported by their approaching an orthogonal orientation with a torsion angle (N1–C1–C2–N2) of −74.16(15)°, as well as a backbone C1–C2 distance of 1.5224(15) Å that corresponded to an isolated C(sp$^2$)–C(sp$^2$) single bond [25]. All other bond lengths and angles in the structure of **2** correspond to those of similar free α-diimines [14, 26].

Crystals of **2** were composed of stacks of individual molecules of **2** engaged in short-contact C–H van der Waal's interactions. Neighboring stacks of **2** participated in weak intermolecular C–H···O hydrogen bonding between a methyl hydrogen (C21H) and a methoxy group oxygen (O2) with a H···O distance of approximately 2.5 Å, a C21–O2 distance of 3.454(2) Å, and a C21–H···O2 bond angle of 154.91(2)°.

**3.2.2. Molecular structure and crystal packing of 4.** The asymmetric unit of **4** consisted of two independent molecules of the metal complex as well as a molecule of dichloromethane. Complexation resulted in the diimine core of **2** adopting an essentially planar configuration, with N1–C1–C2–N2 and N3–C29–C30–N4 torsion angles of 0.01(12)° and 6.64(12)°, respectively. A small degree of delocalization in the diimine core was indicated by four N–C bond lengths equivalent to N1–C1 in the range 1.2990(12)–1.3015(11) Å, as well as C1–C2 and C29–C30 with lengths of 1.4818(12) and 1.4870(12) Å. These bond lengths were correspondingly longer and shorter than those in the free ligand. The delocalization observed in the diimine center of **4** was similar to that observed in related compounds [27, 28].

Deviations in the square-planar geometry of the palladium center of **4** were attributed to the small, 79.61(3)° (N2–Pd1–N1) and 79.15(3)° (N4–Pd2–N3), bite angle of the diimine

Table 2. Selected bond lengths (Å) and angles (°) for **2** and **4**.

| | | | |
|---|---|---|---|
| **2** | | | |
| O1–C18 | 1.3724(14) | O1–C21 | 1.4358(16) |
| C16–C17 | 1.3927(17) | C17–C18 | 1.3854(18) |
| N1–C15 | 1.4186(15) | N1–C1 | 1.2792(15) |
| C1–C2 | 1.5224(15) | N2–C2 | 1.2820(15) |
| N2–C22 | 1.4198(15) | C1–C3 | 1.4884(15) |
| C3–C4 | 1.3991(16) | C4–C5 | 1.3797(17) |
| C18–O1–C21 | 116.99(9) | C16–C15–N1 | 124.39(11) |
| C1–N1–C15 | 122.66(10) | N1–C1–C3 | 118.36(10) |
| N1–C1–C2 | 123.09(10) | C15–N1–C1–C3 | −179.21(9) |
| N1–C1–C2–N2 | −74.16(15) | C3–C1–C2–C9 | −79.12(12) |
| **4** | | | |
| Pd1–N2 | 2.0150(8) | Pd1–N1 | 2.0269(8) |
| Pd2–N3 | 2.0200(8) | Pd2–N4 | 2.0154(8) |
| Pd1–Cl1 | 2.2717(3) | Pd1–Cl2 | 2.2840(2) |
| Pd2–Cl3 | 2.2937(3) | Pd2–Cl4 | 2.2847(3) |
| N1–C1 | 1.3015(11) | N2–C2 | 1.2992(12) |
| N3–C29 | 1.2984(12) | N4–C30 | 1.2990(12) |
| C1–C2 | 1.4818(12) | N2–Pd1–N1 | 79.61(3) |
| C29–C30 | 1.4870(12) | N4–Pd2–N3 | 79.15(3) |
| Cl1–Pd1–Cl2 | 90.171(9) | N2–Pd1–Cl1 | 94.42(2) |
| Cl4–Pd2–Cl3 | 89.368(10) | N4–Pd2–Cl3 | 96.71(2) |
| N1–Pd1–Cl2 | 95.74(2) | N1–C1–C2 | 114.70(8) |
| N3–Pd2–Cl4 | 95.16(2) | N3–C29–C30 | 114.17(8) |
| N2–C2–C1 | 115.63(8) | C1–N1–Pd1 | 114.49(6) |
| N4–C30–C29 | 114.98 | C29–N3–Pd2 | 115.09(6) |
| C2–N2–Pd1 | 114.44(6) | Cl2–Pd1–N2–C2 | −18.06(2) |
| C30–N4–Pd2 | 115.22(6) | Cl4–Pd2–N3–C29 | −173.24(6) |
| Cl1–Pd1–N1–C1 | 3.73(2) | Cl3–Pd2–N4–C30 | 166.47(6) |

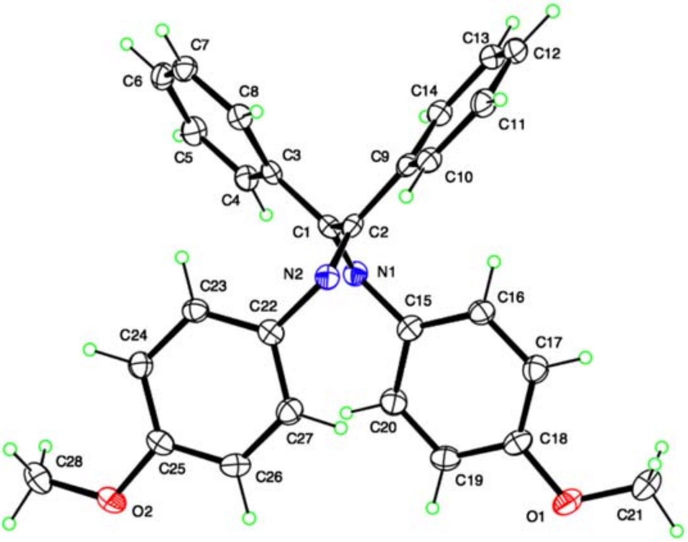


Figure 1. *ORTEP* view of **2**. Ellipsoids are represented at the 50% probability level.

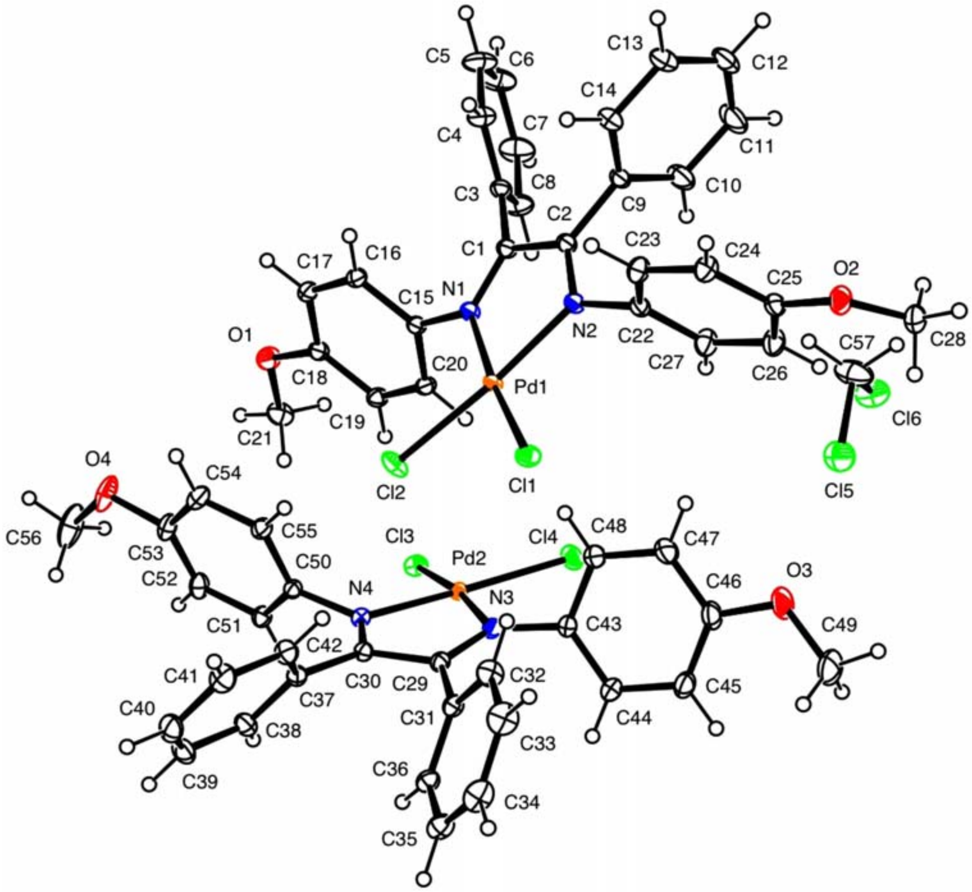


Figure 2. *ORTEP* view of **4**. Ellipsoids are represented at the 50% probability level.

chelates, smaller than the ideal value of 90° for square-planar geometry. Other angles around the palladium approached 90°, for example, 90.171(9)° for Cl1–Pd1–Cl2 and 89.368(10)° for Cl4–Pd2–Cl3, as well as four N–Pd–Cl angles equivalent to N2–Pd1–Cl1 that ranged from 94.42(2) to 96.71(2)°. Distortions in the square-planar geometry of **4** were also observed in the torsion angles Cl2–Pd1–N2–C2, Cl1–Pd1–N1–C1, Cl4–Pd2–N3–C29, and Cl3–Pd2–N4–C30, which deviate from planarity and were, respectively, −18.06(2), 3.73(2), −173.24(6), and 166.47(6)°. Deviations observed in the metal geometry of **4** have been observed in similar compounds [14, 27].

The average length of the $C_{ar}$–O bond in **4** was 1.3622 Å, slightly shorter than the average $C_{ar}$–O bond length of 1.3714 Å in **2** as well as the reported average $C_{ar}$–O bond length of 1.370 Å for alkyl aromatic ethers [25]. The shortening of the $C_{ar}$–O bond in **4** was seen as an indication of the increased resonance interaction of the strongly electron-donating methoxy group upon complexation. This observation would offer insight into the assignments of the bands in the electronic absorption spectrum of **4**.

As in related metal complexes, the *N*-phenyl rings of **4** were at an angle to the palladacycle at its core. One molecule of **4** in the unit cell had its *N*-phenyl rings at angles of

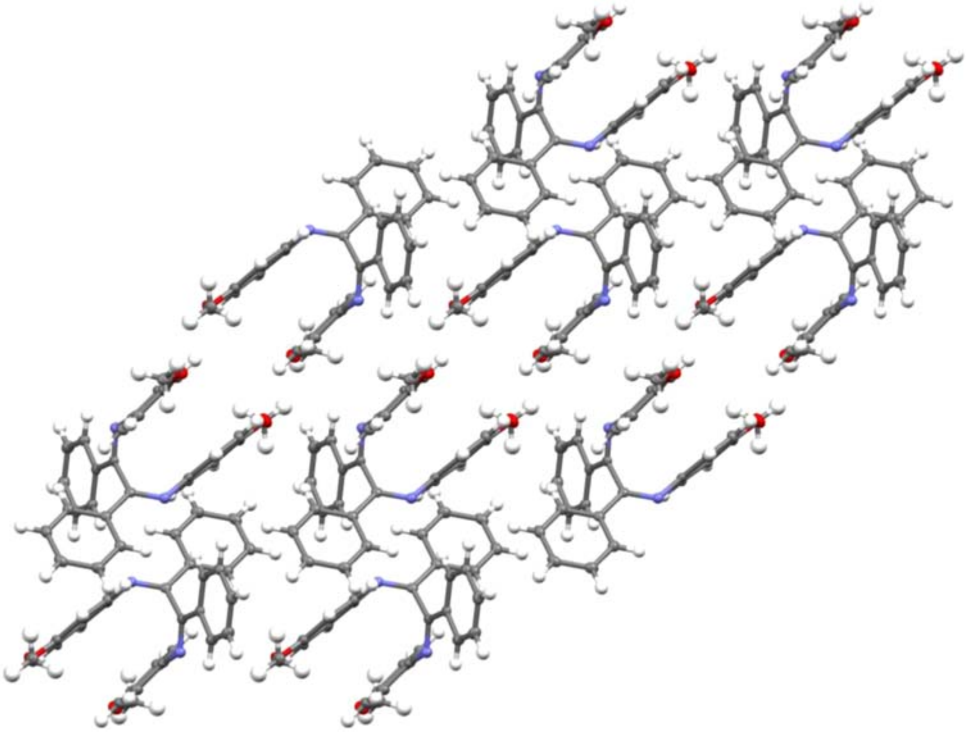


Figure 3. Crystal packing in **2** as viewed along the crystallographic *a*-axis.

86.21(2)° (C22–C27) and 61.35(2)° (C15–C20) to the ideal plane of its palladacycle (Pd1–N1–C1–C2–N2), while the other had its *N*-phenyl rings at 73.73(2)° (C43–C48) and 75.04 (2)° (C50–C55) to the ideal plane of its palladacycle (Pd2–N3–C29–C30–N4) [27, 29].

Crystals of **4** were composed of individual molecules of **4** that interacted via two different modes of hydrogen bonding to form layers. The first type of hydrogen bonding was between H55 and Cl2, with a H···Cl distance of 2.8 Å, a C55–Cl2 distance of 3.708(2) Å and a C55–H···Cl2 bond angle of 161.29(2)° A similar interaction occurred between H19 and Cl3. The second type of hydrogen bonding was a C–H···$\pi$ interaction between a methyl hydrogen (C21H) and the $\pi$-system of a phenyl ring (C50–C55), with a H···ring centroid distance of 2.8 Å, a C21-ring centroid distance of 3.6842(2) Å and a C21–H···ring centroid bond angle of 148.48(2)°.

Molecules of dichloromethane between the layers of **4** served to link them together via two types of intermolecular interactions. The first type was a hydrogen bonding interaction between H27 and Cl6, with a H···Cl distance of 2.9 Å, a C27–Cl6 distance of 3.681(2) Å and a C27–H···Cl6 bond angle of 146.59(2)°. A similar interaction occurred between H57 and Cl4. The second type was a short-contact van der Waal's interaction between Cl5 and O3 with a distance of 3.014(2) Å.

The bond angles and lengths that were observed in **4** were similar to related complexes found in the literature [14, 26–29].

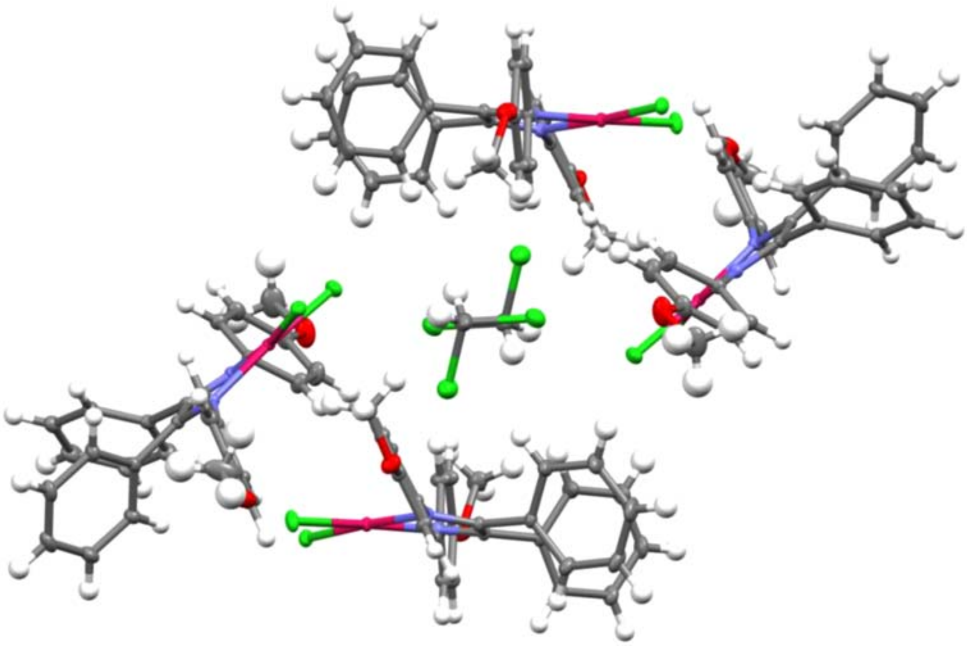


Figure 4. Crystal packing in **4**.

### 3.3. *Electronic absorption spectra of 1–4*

The color difference of **3** and **4**, with the former being a dark orange and the latter being a deep crimson, prompted an investigation of their electronic absorption spectra as well as those of their precursor ligands. Electronic absorption spectral data for **1**–**4** in chloroform (a noncomplexing solvent) are compared in table 3 and presented in figures 5 and 6.

Compounds **1** and **2** had similar absorption spectra with features observed in the spectra of other diimines, specifically, a longer wavelength band near 340–350 nm that was assigned to a $n\rightarrow\pi^*$ transition and a more intense band at 250–300 nm assigned to a $\pi\rightarrow\pi^*$

Table 3. Electronic absorption spectral data for **1–4** in chloroform solution.

| Compound | $\lambda_{max}$ nm (ε)[a] |
|---|---|
| **1** | 269 (28,700)<br>345 (7,220)[b] |
| **2** | 270 (24,900)<br>342 (12,100) |
| **3** | 306 (12,300)<br>405 (9,420) |
| **4** | 280 (8,580)[b]<br>328 (9,450)<br>408 (6,960)<br>518 (3,680)[b] |

[a] Extinction coefficient units $M^{-1}\,cm^{-1}$.
[b] Shoulder.

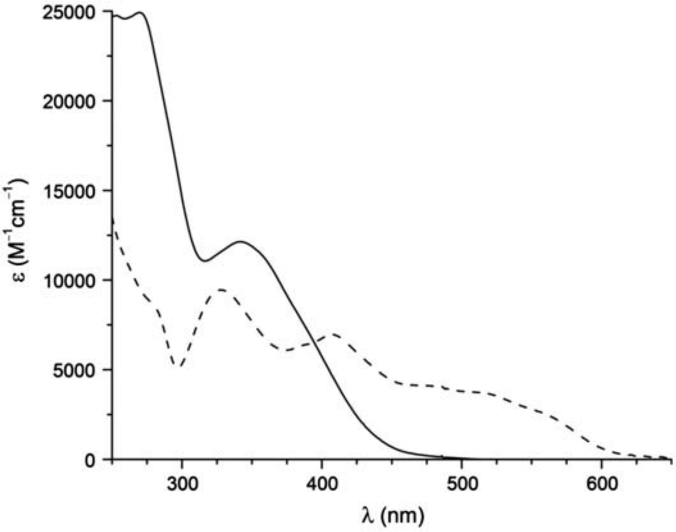


Figure 5. Room temperature electronic absorption spectra for **2** (—) and **4** (- - -) in chloroform solution.

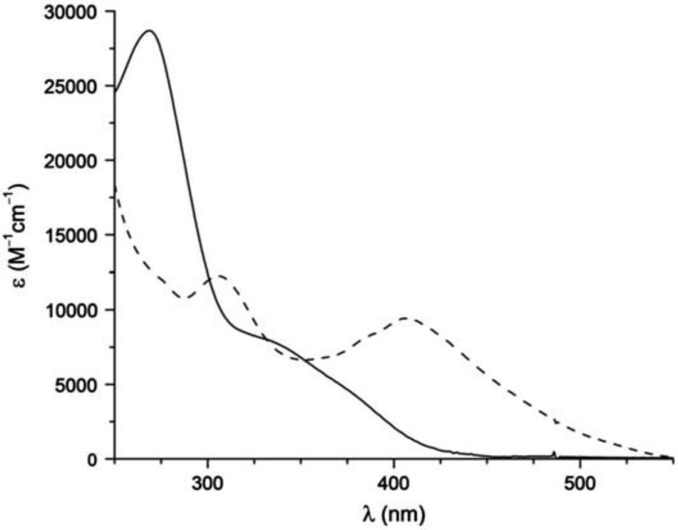


Figure 6. Room temperature electronic absorption spectra for **1** (—) and **3** (- - -) in chloroform solution.

transition [30, 31]. The longer wavelength band in **2**, with an extinction coefficient (ε) of 12,100 M$^{-1}$ cm$^{-1}$, was more intense than its counterpart in **1** that had an extinction coefficient of 7220 M$^{-1}$ cm$^{-1}$. This difference was attributed to the longer wavelength band in the spectrum of **2** having some charge transfer characteristics [7, 32].

Absorption spectra of **3** and **4** in chloroform had two bands at 300–400 nm, with the longer wavelength band being less intense. These bands were assigned to ligand-centered transitions that were red-shifted due to complexation [30]. An additional broad, lower intensity band (ε = 3680 M$^{-1}$ cm$^{-1}$) with a shoulder at 518 nm was observed in the spectrum of **4**, and was seen as the main contributor to its intense color. This band was attributed to a combination of charge transfer transitions, such as $d_\pi(Pd)\rightarrow\pi^*$ and $n(Cl)\rightarrow\pi^*$, that have been red-shifted by the strongly electron-donating methoxy groups on the diimine ligand of **4** [7, 31, 33].

## 4. Conclusion

Two α-diimine ligands were prepared, **1** with bromo groups on two of its phenyl rings and **2** with methoxy groups on two of its phenyl rings. Compounds **1** and **2** were used to prepare palladium(II) complexes, **3** and **4**, respectively. The X-ray structure of **2** revealed unconjugated C–N double bonds in the (*E*)-configuration, while that of **4** showed a diimine core with a degree of conjugation and a nonideal square-planar geometry around palladium caused by the small bite angle of the diimine. Solution-phase electronic absorption spectra of **1** and **2** in chloroform had two main bands arising from $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions. Absorption spectra of **3** and **4** in chloroform solution had bands that were attributed to ligand-centered transitions. The absorption spectrum of **4** featured an additional band with a shoulder at 518 nm that was assigned to a combination of $d_\pi(Pd)\rightarrow\pi^*$ and $n(Cl)\rightarrow\pi^*$ transitions.

## Supplementary material

$^1$H and $^{13}$C NMR spectra of compound **4**, with expansions of the aromatic region, are provided.

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