Adducts of Rhodium(II) Acetate and Rhodium(II) Pivalate with 1,8-Diazabicyclo[5.4.0]undec-7-ene

Eric D. Fussell and Ampofo Darko *

Department of Chemistry, University of Tennessee at Knoxville, 1420 Circle Drive, Knoxville, TN 37996, USA; eridfuss@ut.utm.edu
* Correspondence: adarko@utk.edu

Abstract: In this article, we describe the synthesis of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) adducts of rhodium(II) carboxylate complexes, [Rh$_2$(μ-O$_2$CCR$_3$)$_4$(DBU)$_2$] (R = H (1), Me (2)). The DBU ligand is coordinated to the axial site in both adducts via the imido-nitrogen atom, and single-crystal X-ray diffraction analysis of 1 and 2 revealed structurally similar attributes between the compounds. The Rh–Rh bond distance is 2.4108(3) Å for 1 and 2.4143(2) Å for 2. The Rh–N distance is 2.2681(3) Å for compound 1 and 2.2587(10) Å for compound 2. Compound 1, however, crystallized with solvent molecules in its unit cell, and Hirshfeld surface analysis showed intermolecular C–H···O interactions between oxygen atoms of [Rh$_2$(μ-O$_2$CCR$_3$)$_4$] and the hydrogen of the chloroform solvent among other intermolecular close-contact interactions. The crystal structure of compound 2 was found to be devoid of solvent and showed weak intramolecular C–H···O interactions from the DBU axial ligand to the oxygens of the bridging acetates. Otherwise, Hirshfeld analysis showed that 2 was dominated by H···H interactions. UV-vis spectroscopy of both adducts was also conducted in different solvents to examine shifts attributed to the π*(Rh$_2$) to σ*(Rh$_2$) band.

Keywords: rhodium carboxylate; axial ligand; DBU

1. Introduction

Rhodium(II) paddlewheel complexes [(Rh(II))] are an exceptionally diverse group of bimetallic scaffolds. These compounds have primarily been employed in catalysis to facilitate carbene mediated reactions [1,2], though they have also seen promising use in a variety of other applications such as potential anti-tumor drugs [3–5], sensors [6–9], and scaffolds for supramolecular assemblies [10–12]. Their ability to readily dissolve in most solvents while also maintaining air and moisture stability has certainly served to increase their utility over other transition metal scaffolds. Rh(II) complexes have been demonstrated to perform stereoselective reactions at rates comparable to enzymes [13,14], and these superb kinetic properties allow them to fit into the classification of a “catalytically perfect” chemzyme [15,16].

In general, Rh(II) complexes consist of four equatorial ligands that bridge the dirhodium core and two axial ligands that occupy the remaining coordination site on each rhodium atom (Figure 1). The equatorial units can be exchanged for a variety of other ligands to either influence the compound’s steric environment or to adjust the electron density within the metal core [17,18]. Ligand substitution at the equatorial sites often requires high boiling temperatures and long reaction times, while axial ligand exchange is more facile and occurs quickly at room temperature. Ligands bound to the axial site of the complex have comparatively increased lability and can readily dissociate to form coordinatively unsaturated sites on the metal, depending on the nature of their σ donating or π accepting capabilities. Due to the facile nature of axial ligands, Rh(II) complexes are usually structurally reported as adducts, and only one Rh(II) complex has been reported without axial ligands [19]. Nitrogenous ligands generally display a strong affinity for axial sites, and make up a large majority of Rh(II) tetracarboxylate adducts [18]. Among the bevy of axial
nitrogenous ligands, it is surprising that 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) has yet to be reported as an axial coordinated ligand to a Rh(II) complex. To fill this gap, we report on the synthesis, crystal structures, and UV-vis analysis of DBU adducts of rhodium(II) acetate and rhodium(II) pivalate.

Figure 1. General structural motif for Rh(II) carboxylate adducts (left) and their newly reported derivatives herein (right).

2. Materials and Methods

2.1. General Information

[Rh₂(μ-O₂CCH₃)₄] was purchased from Pressure Chemical Company (Pittsburgh, PA, USA) and used as received. DBU, absolute ethanol, and tetrahydrofuran (THF) were obtained from Fisher Scientific (Pittsburgh, PA, USA) and used without further purification. [Rh₂(μ-O₂CCMe₃)₄] was synthesized according to a literature procedure [20]. ¹H and ¹³C NMR data were obtained at the University of Tennessee (Knoxville, TN, USA) on a 500 MHz Varian spectrometer with CDCl₃ as the solvent. Chemical shifts were referenced to residual CHCl₃ (δ = 7.26 ppm). The UV-vis experiments were collected at the University of Tennessee (Knoxville, TN, USA) on a Cary 3000 spectrophotometer at 1.5 mM solutions of the complexes in various solvents in a 3mL quartz cuvette (1 cm path length). Elemental analysis was carried out by Atlantic Microlab Inc (Norcross, GA, USA).

2.2. Synthesis

Synthesis of [Rh₂(μ-O₂CCH₃)₄(DBU)₂] (1)
A mixture of [Rh₂(μ-O₂CCH₃)₄] (100 mg, 0.226 mmol) was dissolved in 3.0 mL of THF with stirring. DBU (687 mg, 4.53 mmol) was added to the clear, teal solution. After stirring for 15 min, the resulting red-purple precipitate was filtered, washed three times with THF, and dried overnight under vacuum at 30 °C to yield 1 as a red-pink powder (159 mg, 0.213 mmol, 94% yield). ¹H NMR (500 MHz, CDCl₃) δ 3.96 (s, 4H), 3.52 (t, J = 6.1 Hz, 4H), 3.42 (s, 4H), 2.97–2.88 (m, 4H), 2.16 (p, J = 5.9 Hz, 4H), 1.83 (s, 12H), 1.80 (s, 4H), 1.70 (s, 8H), ¹³C NMR (126 MHz, CDCl₃) δ 190.96, 165.98, 53.81, 49.19, 44.84, 35.40, 30.15, 28.67, 26.21, 23.86, 22.91. Anal. Calculated for C₅₆H₄₄N₄: C, 41.83; H, 5.94; N, 7.51. Found: C, 42.04; H, 6.10; N, 7.55.

Synthesis of [Rh₂(μ-O₂CCMe₃)₄(DBU)₂] (2)
[Rh₂(μ-O₂CCMe₃)₄] (100 mg, 0.164 mmol) was dissolved in 3.0 mL of absolute EtOH with stirring. DBU (498 mg, 3.28 mmol) was added and the solution was stirred for 15 min. The precipitate formed was filtered, washed three times with EtOH, and dried overnight under vacuum at 30 °C to yield 2 as a red-pink powder (124 mg, 0.226 mmol, 83% yield). ¹H NMR (500 MHz, CDCl₃) δ 3.72 (dd, J = 7.4, 3.9 Hz, 4H), 3.45 (t, J = 6.2 Hz, 4H), 3.42–3.35 (m, 4H), 2.98–2.90 (m, 4H), 2.05 (p, J = 6.1 Hz, 5H), 1.79 (s, 4H), 1.71 (s, 9H), 0.92 (s, 36H), ¹³C NMR (126 MHz, CDCl₃) δ 197.62, 165.10, 53.34, 49.13, 44.71, 40.04, 35.40, 30.15, 28.67, 26.21, 23.86, 22.91. Anal. Calculated for C₃₈H₆₈N₄: C, 49.89; H, 7.49; N, 6.12. Found: C, 50.12; H, 7.56; N, 6.26.
2.3. Single-Crystal X-ray Diffraction Analysis

Single crystals of 1 and 2 suitable for single-crystal X-ray diffraction analysis were obtained by slow diffusion of hexanes into a chloroform solution of 1 or 2 at room temperature. Single-crystal X-ray diffraction data were collected on a Bruker APEX-II CCD diffractometer with a Mo Kα radiation source (λ = 0.71073 Å) at 100.0 K. Using Olex2 [21], the structures were solved with the olex2.solve [22] structure solution program using charge flipping and refined with a SHELXL refinement package [23] using least squares minimization. Hydrogen atom locations were calculated and refined as riding models, while all other atoms were refined using anisotropic displacement. A summary of the crystal and refinement data can be found in Table 1. Additional crystal structure data can be found in the supplementary materials in Tables S1–S7. CCDC 2070090-2070091 contain the crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

| Table 1. Crystal data and structural refinements for compounds 1 and 2. |
|-------------------------------------------------|
| Compound | [Rh$_2$(μ-O$_2$CCH$_3$)$_2$(DBU)$_4$·4CHCl$_3$] (1·4CHCl$_3$) | [Rh$_2$(μ-O$_2$CCMe)$_2$(DBU)$_2$] (2) |
| Empirical formula | C$_{68}$H$_{48}$Cl$_{2}$N$_{15}$O$_{15}$Rh$_2$ | C$_{68}$H$_{48}$N$_{15}$O$_{15}$Rh$_2$ |
| Formula weight | 1228.0 | 914.78 |
| Crystal system | triclinic | triclinic |
| Space group | P-1 | P-1 |
| α/Å | 11.4507(16) | 10.5113(7) |
| β/Å | 14.1185(19) | 10.8561(7) |
| γ/Å | 15.891(2) | 11.0178(7) |
| Volume/Å$^3$ | 2332.1(5) | 11611.2(2) |
| Z | 2 | 1 |
| ρcalc/g/cm$^3$ | 1.743 | 1.399 |
| μ/mm$^{-1}$ | 1.443 | 0.910 |
| F(000) | 1228.0 | 487.0 |
| Crystal size/mm$^3$ | 0.18 × 0.11 × 0.08 | 0.26 × 0.25 × 0.15 |
| Radiation | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2θ range for data collection/° | 4.34 to 63.096 | 4.208 to 63.094 |
| Index ranges | -16 ≤ h ≤ 16, -20 ≤ k ≤ 20, -23 ≤ l ≤ 23 | -15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -16 ≤ l ≤ 16 |
| Reflections collected | 33,345 | 55,863 |
| Independent reflections | 15457 [Rint = 0.0353, Rsigma = 0.0471] | 7209 [Rint = 0.0407, Rsigma = 0.0200] |
| Data/restraints/parameters | 15,457/0/509 | 7209/0/272 |
| Goodness-of-fit on F$^2$ | 1.044 | 1.064 |
| Final R indices [I > 2σ(I)] | R1 = 0.0378, wR2 = 0.0798 | R1 = 0.0213, wR2 = 0.0473 |
| Final R indexes [all data] | R1 = 0.0550, wR2 = 0.0908 | R1 = 0.0263, wR2 = 0.0499 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.36/−2.21 | 0.43/−0.87 |

3. Results and Discussion

3.1. Synthesis and Characterization of 1 and 2

Adducts 1 and 2 were obtained by adding an excess of DBU to the respective rhodium (II) starting complex in THF or ethanol. The products precipitate quickly and were recovered by filtration after 15 min of stirring. The products were further purified by recrystallization by slow diffusion of hexanes into a chloroform solution of 1 or 2.

The products were characterized using $^1$H NMR, $^{13}$C NMR, and elemental analysis. Adduct 1’s $^1$H NMR was measured in CDCl$_3$ and showed a singlet at 1.83 ppm, which was assigned to the protons on the methyl group of bridging acetates (Figure S3). All of the DBU methylene units appeared as expected in its $^1$H NMR, with the pivalate protons appearing as a sharp singlet at 0.92 ppm, while the methylene protons of the DBU units appear between the range of 1.71–3.73 ppm (Figure S5). The $^{13}$C NMR of 2 (Figure S6) is also similar to that

...
of 1, with the carboxylate carbon of the pivalate at 197.62 ppm. The amidine carbon of DBU is located at 165.10 ppm. The remaining carbons from the methylene units of DBU and the quaternary and methyl portions of the pivalate tert-butyl groups appear between 23.09–53.34 ppm. The methyl carbons of the pivalate groups show an intense signal at 27.99 ppm.

3.2. Crystal Structures of 1 and 2

The structures of the two complexes were obtained by single-crystal X-ray diffraction and showed the DBU ligand to be coordinated through the imido-nitrogen as well as displaying various inter- and intramolecular hydrogen bonding interactions. Compound 1 crystallized as a chloroform solvate (1·4CHCl₃, see Figure S1 for the asymmetric unit) and the obtained crystal structure (Figure 2) clearly shows two DBU compounds coordinated to each of the paddlewheel’s axial sites. Table 2 lists selected bond angles and bond lengths from this structure. DBU binds to the Rh axial site through the lone pair of its sp² hybridized nitrogen similarly to how pyridine has been reported to bind to rhodium acetate [24]. The resulting Rh–N bond length of 2.2681(3) Å is slightly elongated compared to the pyridine adduct’s Rh–N bond of 2.227(2) Å, likely due to differences in planarity between them and added steric bulk from DBU’s fused seven membered ring. This steric bulk also causes the DBU’s Rh–Rh–N bond to slightly deviate from linearity, yielding a bond angle of 176.55°. This bond angle indicates that the rhodium atom cannot attain perfect octahedral molecular geometry, resulting in a slightly distorted geometry. The Rh–Rh bond length of the bis-DBU adduct (2.4108(3) Å) is also longer compared to the bis-pyridyl adduct (2.3963(2) Å). Like the pyridines in the aforementioned adduct, each DBU orients along the bridging acetates’ clefts to reduce steric repulsion.

![Figure 2. Single crystal X-ray structure of [Rh₂(µ-O₂CCMe₃)₄(DBU)₂]·4CHCl₃ (1·4CHCl₃). One of the asymmetric unit’s two Rh(II) adducts is shown. The thermal ellipsoids are shown at 50% probability with selected hydrogen atoms.](image)

The [Rh₂(µ-O₂CCMe₃)₄(DBU)₂] (2) crystal structure (Figure 3) gives insight into the effects of equatorial ligand bulk on solvent interactions (see Figure S2 for the asymmetric unit). This is similar to 1 in that the axial DBU units bind in a staggered fashion, resting between the equatorial carboxylate ligands. The major difference between the two adducts is that adduct 2 has bulky tert-butyl groups at the equatorial ligands and the enhanced steric bulk of these ligands seems to influence the Rh–Rh–N bond angle. The steric repulsion between these ligands and the protruding seven membered ring of the DBU induces a more pronounced perturbation of this angle to 172.39°, causing the geometry about the rhodium to deviate even further from the optimal octahedral geometry than adduct 1. Despite the
increased distortion in the ligand field about rhodium, the Rh–N bond length of 2.2587(10) Å is shorter than that of the acetate adduct. The Rh–Rh bond, though, is very similar to the acetate adduct at 2.4143(2) Å.

Table 2. Selected bond lengths and dihedral angles from the XRD data.

| Bond Set | Bond | [Rh2(µ-O2CCH3)4(DBU)2]·4CHCl3 | [Rh2(µ-O2CCMe3)4(DBU)2] |
|----------|------|-------------------------------|-------------------------|
|          | Rh1–Rh1 | 2.4108(3)                      | 2.4143(2) |
|          | Rh1–O1  | 2.0450(2)                      | 2.0515(9) |
|          | Rh1–O4  | 2.0376(3)                      | 2.0272(9) |
|          | Rh1–N1  | 2.2681(3)                      | 2.2587(10) |
|          | N1–C9   | 1.3010(4)15                   | 1.2922(15) |
|          | C9–N2   | 1.3620(2)16                   | 1.3679(15) |

| Bond Set | Dihedral Angle (°) | Dihedral Angle (°) |
|----------|--------------------|--------------------|
|          | Rh1–Rh1–O1         | 88.28(5)           | 87.46(3) |
|          | Rh1–Rh1–O4         | 88.54(5)           | 87.83(3) |
|          | Rh1–Rh1–N1         | 176.55(6)          | 172.39(3) |
|          | O4–Rh1–O3          | 175.74(7)          | 175.65(4) |
|          | O4–Rh1–O1          | 87.79(7)           | 89.23(4) |
|          | O1–Rh1–N1          | 93.69(7)           | 96.40(4) |

Figure 3. Single crystal X-ray structure of [Rh2(µ-O2CCMe3)4(DBU)2] (2). The thermal ellipsoids are shown at 50% probability with selected hydrogen atoms and disordered tert-butyl groups of adduct 2 omitted for clarity.

Hydrogen bonds were found in 1·4CHCl3 and 2 in the form of intramolecular interactions between the DBU axial ligand and the acetate bridging core, and intermolecular interactions with the chloroform solvent molecules in the case of 1·4CHCl3. A summary of the hydrogen-bonding interactions in 1·4CHCl3 and 2 are given in Table 3. In the completed unit cell of complex 1·4CHCl3 we see several hydrogen-bonding type interactions (Figure 4). Intramolecular C–H···O interactions between the DBU axial ligand and the acetate bridging ligands, such as C1–H1B···O3 and C8–H8B···O3, flank the axially coordinated imido nitrogen and could serve to strengthen the DBU coordination. Additional hydrogen bonds are intermolecular C–H···O interactions between chloroform and the bridging acetates such as C17–H17B···O6. Bridging acetates O6 and O2 form bifurcated hydrogen bonds with a C–H group of chloroform molecules and a C–H from DBU. Looking more closely at the bifurcated interactions at O6, the interactions are relatively symmetrical: C17–H17B···O6 = 3.21 Å and C29–H29···O6 = 3.32 Å. There are also cases where the H in chloroform is bifurcated, such as in C27–H27 which interacts with O1 and O4. Close contacts between DBU and the Cl of chloroform were also identified, but these were over comparatively longer distances than the C–H···O interactions: C1–H1A···Cl3 = 3.87 Å, C7–H7A···Cl11 = 3.83 Å, and C16–H16A···Cl11 = 3.77 Å. Compound 2 only displayed...
intramolecular C–H···O interactions between a C–H on the DBU ligand and the bridging ligand as shown in Figure 3: C8–H8A···O1.

Table 3. Selected C–H···O and C–H···Cl interactions for complexes 1·4CHCl₃ and 2.

|               | D–H (Å) | H···A (Å) | D···A (Å) | ∠D–H···A (°) |
|---------------|---------|---------|---------|-------------|
| **Compound 1**|         |         |         |             |
| C27–H27···O1  | 1.00    | 2.57    | 3.41    | 141.8       |
| C1–H1B···O2   | 0.99    | 2.54    | 3.21    | 124.6       |
| C8–H8B···O3   | 0.99    | 2.27    | 3.21    | 157.4       |
| C27–H27···O4  | 1.00    | 2.49    | 3.23    | 130.2       |
| C1–H1A···Cl3  | 0.99    | 2.93    | 3.87    | 159.6       |
| C28–H28···O2  | 1.00    | 2.27    | 3.12    | 141.9       |
| C28–H28···O3  | 1.00    | 2.59    | 3.33    | 130.4       |
| C7–H7A···Cl1  | 0.99    | 2.92    | 3.83    | 153.2       |
| C30–H30···O5  | 1.00    | 2.46    | 3.18    | 128.6       |
| C16–H16A···Cl1 | 0.99  | 2.85    | 3.77    | 155.3       |
| C17–H17B···O6 | 0.99    | 2.31    | 3.21    | 151.6       |
| C10–H10B···O7 | 0.99    | 2.51    | 3.21    | 128.1       |
| C29–H29···O7  | 1.00    | 2.31    | 3.18    | 144.3       |
| C29–H29···O6  | 1.00    | 2.51    | 3.32    | 137.4       |

| **Compound 2**|         |         |         |             |
| C8–H8···O1    | 0.99    | 2.55    | 3.30    | 132.7       |

Figure 4. The crystal structure of compound 1. The thermal ellipsoids are shown at 50% probability with selected hydrogen atoms omitted for clarity.

3.3. Hirshfeld Surface Analysis

Hirshfeld surface analyses were obtained to further probe the contributions of the close contacts and other packing interactions in 1·4CHCl₃ and 2. Hirshfeld surfaces, fingerprint maps and void domains were computed from adducts 1 and 2’s crystal data utilizing the CrystalExplorer 17.5 software package [25–27]. The crystal packing of adduct 1·4CHCl₃ mainly consists of H···H interactions at 51.7% of the total interactions, as seen in Figure 5. The interface between the adjacent DBU ligands’ seven membered rings show the highest concentration of these contacts according to the d_{norm} map. Chloroform is also revealed to contribute significantly to the overall packing interactions. The chlorines of chloroform
interact with hydrogens of the adduct through H···Cl close contacts, contributing the second highest percentage of total interactions at 34.2%. Beyond this, the chloroform molecules also display bifurcated hydrogen bonding-like interactions with the equatorial acetate ligands’ oxygens, as shown by the dark red spots on the Hirshfeld surface map. These, along with other intermolecular O···H interactions, make up 7.4% of the total interactions. The remaining H···O and C···H/H···C close contacts contribute relatively little to the overall interactions of 1·4CHCl₃, at 1.5 and 2.7%, respectively. The void domain of 1 (Figure 6a) informs that the crystal’s unit cell of 1·4CHCl₃ has a void volume of 273.02 Å³ and a void surface area: 856.97Å². The calculated void percentage was 12%.

Figure 5. Hirshfeld surfaces mapped over dnorm and 2-D fingerprint plots for 1·4CHCl₃ as viewed along the a axis showing (a) all interactions, and delineated into (b) H···H (51.7%), (c) H···Cl (34.2%), (d) O···H (7.4%), (e) H···O (1.5%), (f) C···H/H···C (2.7%), and (g) N···H/H···N (1.2%) interactions. The di and de values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.
Figure 7 reveals that the majority (94.9%) of packing interactions in adduct 2 arises from H···H contacts. The densest of these contacts occur intramolecularly between the hydrogen atoms of adjacent tert-butyl groups. These are observed as the dark red circle at the center of the Hirshfeld surface. This suggests that the crystal is largely held together by favorable London dispersion interactions between the aforementioned tert-butyl groups. The remaining close contacts between O···H/H···O and N···H/H···N contribute little to the total amount of intermolecular contacts at 2.2% and 1.9%, respectively. The void data for 2 (Figure 6b) shows that it has both a smaller void volume (139.55 Å³) and surface area (429.97 Å²) than 1·4CHCl₃. The calculated void percentage of 13% in the crystal of 2 is slightly greater than 1 (12% void percentage), which indicates a negligible difference in packing efficiency.

Figure 6. Void domains and associated data for (a) adduct 1·4CHCl₃ and (b) complex 2.

3.4. Ultraviolet-Visible Spectroscopy

The UV-vis spectra of both Rh(II) adducts 1 and 2 and their electronic responses in various solvent environments were measured. These spectra are displayed in Figure 8. Each set contains the two commonly encountered bands seen in typical Rh(II) paddlewheel complexes. The lower energy band, band A, generally resides between 600 nm–700 nm. This peak appears due to the well-established electronic transition between the HOMO and LUMO of the adduct, the Rh₂(π*) → Rh₂(σ*) transition [28]. The higher energy band B resides in the ~450 nm sector of the visible region. The transitions that give rise to band B can vary depending on the nature of the dirhodium species’ first ligand sphere, thus is not readily identified without thorough computational investigation [29].

The overlaid spectra of 1 in various solvents (Figure 8) shows loose trends about the effect of solvent choice on band location. DCM can be considered the control solvent, as it is the solvent with the lowest donor number [30,31] in the series and therefore the least likely to compete with DBU for the rhodium axial site. In DCM, band A appears at 549 nm while band B is located at 464 nm for complex 1. Solvation of 1 in ethanol (EtOH) shifts band A to the lowest energy (569 nm) of the series, while the adduct in acetonitrile shifts band A to slightly higher energy (548 nm) compared to DCM. The overall trend of band A’s wavelength in 1 was: ACN ≈ DCM < THF ≈ CHCl₃ ≈ DMF < EtOH. In the different solvents, band B was clustered in the range of 451 nm to 464 nm with the highest energy in EtOH (451 nm) and lowest energy in DCM (464 nm). The overall trend was found to be: EtOH < ACN ≈ CHCl₃ < THF ≈ DMF ≈ DCM (see Table S8 for donor numbers of the solvents and wavelengths for the bands of 1 in different solvents).

Figure 9 shows similar findings for adduct 2’s spectra. When the adduct is dissolved in DCM, band A appears at 558 nm and band B is at 460 nm. When solvated in CHCl₃, bands A and B display the same inverse relationship as seen when adduct 1 was dissolved in EtOH. Band A appears at the highest wavelength in the series at 591 nm, while band B...
appears at the lowest wavelength of 445 nm. In addition, the molar attenuation coefficient of each band is drastically increased as compared to the adduct response in DCM. The overall trend of band A’s wavelengths is ACN < THF = DCM ≈ DMF < EtOH < CHCl₃ while band B’s wavelengths are in the order of CHCl₃ < EtOH = ACN ≈ DCM ≈ THF < DMF (see Table S9 for donor numbers of the solvents and wavelengths for the bands of 2 in different solvents).

Comparing the trends of the adducts reveals interesting findings. Band A was recorded to be at the highest energy when ACN was the solvent in the case of both 1 and 2, but there was a larger shift compared to DCM with complex 2. The shift of band A was only negligible when complex 1 was in ACN compared to DCM. It is possible that in solution, DBU is less tightly associated in complex 2 than 1, which allows ACN to better compete with DBU for axial site occupancy. ACN is a sterically unhindered nitrogenous donor, which primes it to form stronger bonds to the rhodium axial site than DBU due to the reduced steric bulk of the former. Once it replaces DBU, more electron density can be donated into the dirhodium core, which increases the energy of the π*(Rh₂) to σ*(Rh₂)
transition. Because this transition is responsible for band A, it results in a blue shift when compared to the DBU coordinated complex.

Figure 8. UV-vis spectrum showing the molar attenuation coefficient of 1 in various solvents.

Figure 9. UV-vis spectrum showing the molar attenuation coefficient of 2 in various solvents.

The case for a less tightly bound DBU in solution for 2 can also be rationalized by considering trends with CHCl₃ as the solvent. Despite its low coordinating ability, CHCl₃ shifts band A of 1 and 2 to lower energy. The difference in shifts in CHCl₃ when compared to DCM is much greater for complex 2 than complex 1 (33 nm shift for 2 vs 8 nm shift for 1). DBU has been used as a base promoter for the addition of CHCl₃ to carbonyl compounds [32,33], so it is possible that a weaker association to Rh allows DBU to interact with CHCl₃, thereby freeing the axial sites. As a weaker electron donor, CHCl₃ bound to the rhodium (II) axial site decreases the π*(Rh₂) to σ*(Rh₂) energy gap, ultimately shifting
the energy of band A to a lower energy area of the spectrum [28,34,35]. As in with ACN, the reason CHCl₃ does not show a drastic change to the wavelength of adduct 1 likely resides in a tighter Rh-DBU association in solution than in adduct 2.

4. Conclusions

The novel [Rh₂(μ-O₂CCH₃)₄(DBU)] (1) and [Rh₂(μ-O₂CCMe₃)₄(DBU)] (2) adducts were successfully synthesized and characterized. In both cases, axial coordination occurs through the most basic imido-nitrogen of DBU. Their structural characteristics were described here by single-crystal XRD crystallography in which intra- and intermolecular hydrogen bonding interactions were found. Complex 1 crystallized as a solvate and had a more diverse set of hydrogen bonding interactions, while solid state interactions in 2 were much simpler. Hirshfeld surface analysis supported these findings. UV-vis analysis in different solvents demonstrated that DBU has a weaker coordination in complex 2 due to the observations of shifts of absorption bands in acetonitrile and chloroform solvents. Investigation of how the differences between complex 1 and 2 manifest in their reactivity is the subject of further study in our lab.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/cryst11050517/s1, Figure S1: Asymmetric unit of compound 1·4CHCl₃, Figure S2: Asymmetric unit of compound 2, Figure S3: 500 MHz ¹H NMR spectra of 1, Figure S4: 500 MHz ¹³C NMR spectra of 1, Figure S5: 500 MHz ¹H NMR spectra of 2, Figure S6: 500 MHz ¹³C NMR spectra of 2, Table S1: Bond lengths for 1·4CHCl₃, Table S2: Bond angles for 1·4CHCl₃, Table S3: Torsion angles for 1·4CHCl₃, Table S4: Bond lengths for 2, Table S5: Bond angles for 2, Table S6: Torsion angles for 2, Table S7: Atomic occupancy for 2, Table S8: UV-vis data for 1 in various solvents Table S9: UV-vis data for 2 in various solvents.

Author Contributions: Conceptualization, E.D.F. and A.D.; methodology, E.D.F.; formal analysis, E.D.F.; investigation, E.D.F.; resources, E.D.F. and A.D.; data curation, E.D.F.; writing—original draft preparation, E.D.F.; writing—review and editing, E.D.F. and A.D.; visualization, E.D.F. and A.D.; supervision, A.D.; project administration, A.D.; funding acquisition, E.D.F. and A.D. All authors have read and agreed to the published version of the manuscript.

Funding: We are grateful to the University of Tennessee Graduate School’s Student Faculty Research Award for funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data presented in this study are available as additional supporting information in the form of raw UV-vis and NMR files.

Acknowledgments: The authors wish to thank Xian Carroll for assistance with the single-crystal X-ray diffraction analysis and David Jenkins for helpful discussions. The authors also acknowledge Ziling (Ben) Xue, Anthony Abshire, and Autumn Giles for assistance with proofreading.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Hansen, J.; Davies, H.M.L. High symmetry dirhodium(II) paddlewheel complexes as chiral catalysts. Coord. Chem. Rev. 2008, 252, 545–555. [CrossRef]
2. Snyder, J.P.; Padwa, A.; Stengel, T.; Arduengo, A.J.; Jockisch, A.; Kim, H.-J. A Stable Dirhodium Tetracarboxylate Carbenoid: Crystal Structure, Bonding Analysis, and Catalysis. J. Am. Chem. Soc. 2001, 123, 11318–11319. [CrossRef]
3. de Souza, A.R.; Najjar, R.; Glikmanas, S.; Ber Zyngier, S. Water-soluble rhodium(II) carboxylate adducts: Cytotoxicity of the new compounds. J. Inorg. Biochem. 1996, 64, 1–5. [CrossRef]
4. Katsaros, N.; Anagnostopoulou, A. Rhodium and its compounds as potential agents in cancer treatment. Crit. Rev. Oncol. Hematol. 2002, 42, 297–308. [CrossRef]
5. Rahman, M.M.; Yasuda, H.; Katsura, S.; Mizuno, A. Inhibition of endonuclease cleavage and DNA replication of E. coli plasmid by the antitumor rhodium(II) complex. Arch. Biochem. Biophys. 2007, 464, 28–35. [CrossRef]
6. Hilderbrand, S.A.; Lim, M.H.; Lippard, S.J. Dirhodium tetracarboxylate scaffolds as reversible fluorescence-based nitric oxide sensors. *J. Am. Chem. Soc.* 2004, 126, 4972–4978. [CrossRef]

7. Koo, E.; Yang, L.-H.; Ahn, D.J. A “turn-on” fluorescent microbead sensor for detecting nitric oxide. *Int. J. Nanomed.* 2014, 10, 115–123. [CrossRef] [PubMed]

8. Moragues, M.E.; Esteban, J.; Ros-Lis, J.V.; Martinez-Manez, R.; Marcos, M.D.; Martinez, M.; Soto, J.; Sancenon, F. Sensitive and Selective Chromogenic Sensing of Carbon Monoxide via Reversible Axial CO Coordination in Binuclear Rhodium Complexes. *J. Am. Chem. Soc.* 2011, 133, 15762–15772. [CrossRef]

9. Pannek, C.; Tarantik, K.; Schmitt, K.; Wöllenstein, J. Investigation of Gasochromic Rhodium Complexes Towards Their Reactivity to CO and Integration into an Optical Gas Sensor for Fire Gas Detection. *Sensors* 2018, 18, 1994. [CrossRef] [PubMed]

10. Cotton, F.A.; Lin, C.; Murillo, C.A. Supramolecular Arrays Based on Dimetal Building Units. *Eur. J. Inorg. Chem.* 2010, 15, 3548–3556. [CrossRef]

11. Cotton, F.A.; Hillard, E.A.; Murillo, C.A. The First Dirhodium Tetracarboxylate Molecule without Axial Ligation: New Insight into the Electronic Structures of Molecules with Importance in Catalysis and Other Reactions. *J. Am. Chem. Soc.* 2002, 124, 1014–1023. [CrossRef] [PubMed]

12. Reger, D.L.; Debreczeni, A.; Smith, M.D. Rhodium paddlewheel dimers containing the $\pi \cdots \pi$ stacking, 1,8-naphthalimide supramolecular synth. *Inorg. Chim. Acta* 2011, 378, 42–48. [CrossRef]

13. Adly, F.G.; Ghanem, A. Chiral Dirhodium(II) Carboxylates and Carboxamidates as Effective Chemzymes in Asymmetric Synthesis of Three-Membered Carbocycles. *Chirality* 2014, 26, 692–711. [CrossRef] [PubMed]

14. Pirrung, M.C.; Liu, H.; Morehead, A.T. Rhodium Chemzymes: Michaelis–Menten Kinetics in Dirhodium(II) Carboxylate-Catalyzed Carbene Reactions. *J. Am. Chem. Soc.* 2002, 124, 1014–1023. [CrossRef] [PubMed]

15. Bugg, T. *Introduction to Enzyme and Coenzyme Chemistry*, 2nd ed.; Blackwell Publishing Ltd: Oxford, UK, 1997.

16. Waldrop, M.M. “Chemzymes” Mimic Biology in Miniature. *Science* 1989, 245, 354–355. [CrossRef]

17. Hrdina, R. Dirhodium(II,II) Paddlewheel Complexes. *Eur. J. Inorg. Chem.* 2021, 2021, 501–528. [CrossRef]

18. Cotton, F.A.; Murillo, C.A.; Walton, R.A. Multiple Bonds between Metal. Atoms, 3rd ed.; Springer Science and Business Media: New York, NY, USA, 2005.

19. Cotton, F.A.; Hillard, E.A.; Murillo, C.A. The First Dirhodium Tetracarboxylate Molecule without Axial Ligation: New Insight into the Electronic Structures of Molecules with Importance in Catalysis and Other Reactions. *J. Am. Chem. Soc.* 2002, 124, 5658–5660. [CrossRef]

20. Handa, M.; Nakao, T.; Mikuriya, M.; Kotera, T.; Nukada, R.; Kasuga, K. Chain Complexes of Rhodium(II) Pivalate Dimers Formed by Ligation of C=C Double Bond and Carbonyl Oxygen of p-Quinone [[Rh$_2$(O$_2$CCMe$_3$)$_3$](p-Q)$_2$][Rh$_2$(O$_2$CCMe$_3$)$_3$]$_n$. [CrossRef]

21. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, 42, 339–341. [CrossRef]

22. Bourhis, L.J.; Dolomanov, O.V.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment—Olex2 dissected. *Acta Crystallogr. Sect. C* 2015, 71, 59–75. [CrossRef] [PubMed]

23. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C* 2015, 71, 3–8. [CrossRef] [PubMed]

24. Koh, Y.B.; Christoph, G.G. Metal-Metal Bonding in Dirhodium Tetracarboxylates. Structure of the Bis(pyridine) Adduct of Tetra-µ-aceto-dirhodium(II). *Inorg. Chem.* 1978, 17, 2590–2596. [CrossRef]

25. Spackman, M.A.; Jayatilaka, D. Hirshfeld surface analysis. *CrystEngComm* 2009, 11, 19–32. [CrossRef]

26. Spackman, M.A.; McKinnon, J.J. Fingerprinting intermolecular interactions in molecular crystals. *CrystEngComm* 2002, 4, 378–392. [CrossRef]

27. Turner, M.J.; McKinnon, J.J.; Jayatilaka, D.; Spackman, M.A. Visualisation and characterisation of voids in crystalline materials. *CrystEngComm* 2011, 13, 1804–1813. [CrossRef]

28. Berry, J.F. The role of three-center/four-electron bonds in superelectrophilic dirhodium carbene and nitrene catalytic intermediates. *Dalton Trans.* 2012, 41, 700–713. [CrossRef]

29. Kataoka, Y.; Fukamoto, R.; Yano, N.; Atarashi, D.; Tanaka, H.; Kawamoto, T.; Handa, M. Synthesis, Characterization, Absorption Properties, and Electronic Structures of Paddlewheel-Type Dirhodium(II) Tetra-µ- (n-naphthoate) Complexes: An Experimental and Theoretical Study. *Molecules* 2019, 24, 447. [CrossRef]

30. Gutmann, V. Empirical parameters for donor and acceptor properties of solvents. *Electrochim. Acta* 1976, 21, 661–670. [CrossRef]

31. Gutmann, V. Solvent effects on the reactivities of organometallic compounds. *Coord. Chem. Rev.* 1976, 18, 225–255. [CrossRef]

32. Aggarwal, V.K.; Mereu, A. Amidine-Promoted Addition of Chloroform to Carbonyl Compounds. *J. Org. Chem.* 2000, 65, 7211–7211. [CrossRef]

33. Koyama, M.; Kawakami, T.; Okazoe, T.; Nozaki, K. Cyanide-Free One-Pot Synthesis of Methacrylic Esters from Acetone. *Chem. Eur. J.* 2019, 25, 10913–10917. [CrossRef] [PubMed]

34. Warzecha, E.; Berto, T.C.; Berry, J.F. Axial Ligand Coordination to the C-H Amination Catalyst Rh$_2$(esp)$_2$: A Structural and Spectroscopic Study. *Inorg. Chem.* 2015, 54, 8817–8824. [CrossRef] [PubMed]

35. Warzecha, E.; Berto, T.C.; Wilkinson, C.C.; Berry, J.F. Rhodium Rainbow: A Colorful Laboratory Experiment Highlighting Ligand Field Effects of Dirhodium Tetracate. *J. Chem. Educ.* 2019, 96, 571–576. [CrossRef]