Net Charge Effects in N-Heterocyclic Carbene– Ruthenium Complexes with Similar Oxidation States and Coordination Geometries

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Abstract. A chelating benzimidazolylidene-carboxylate ligand (**1**) was transferred from [Ag(**1**)] to [RuCl₂(dmsu)₄] to afford *trans*(C)-[Ru(**1**)₂(bpy)] (**2**), but all attempts to incorporate **1** into *cis*(Cl)-[RuCl₂(bpy)₂] were unsuccessful. Alternatively, reaction of [RuCl(**1**)(η⁶-cymene)] (**3**) with bpy and AgOTf successfully produced [Ru(**1**)(bpy)₂][OTf] (**4**). Methylation of **2** and **4** with MeOTf yielded *trans*(C)-[Ru(**1-Me**)₂(bpy)][OTf]₂ (**5**) and [Ru(**1-Me**)(bpy)₂][OTf]₂ (**6**), accompanied by a +2 and +1 increase in net charge, respectively. Cyclic voltammetry indicated that the increase in Ru(II)/Ru(III) oxidation potential from **2** to **5** was twice the increase from **4** to **6**. UV–visible spectroscopy also revealed that transitions in **5** occurred at higher energy than in **2** by double the difference between **6** and **4**. Crystallographic analysis demonstrated that the coordination environment of Ru did not differ

significantly between **2** and **5**, suggesting that the observed shifts in oxidation potentials and absorption wavelengths are not due to changes in coordination chemistry or formal oxidation state. Collectively, these results show that **5** and **6** feature Ru centers more electron deficient than those in **2** and **4**, respectively, by amounts proportional to the difference in net charge.

Keywords: chelating anionic N-heterocyclic carbene • bipyridine • ruthenium • net charge effects • methylation

1. Introduction

Transition metal complexes supported by N-heterocyclic carbene (NHC) ligands are routinely employed as catalysts for organic transformation and polymerization reactions [1]. More recently, these complexes have received significant attention for use in chemotherapy [2], dye-sensitized solar cell [3], H₂ storage [4], and CO₂ fixation applications [5]. The structure, bonding and reactivity of an organometallic complex can be strongly influenced by the electron density at the metal center, which in turn is affected by ligand donating ability, metal oxidation state, and net Coulombic charge. Tuning an organometallic complex to achieve specific desired properties or reactivity therefore requires an understanding of how ligand donating ability, oxidation state, and net charge individually contribute to the electron density at a metal center.

We recently reported the synthesis of a chelating benzimidazolylidene-carboxylate ligand and its coordination chemistry with silver and ruthenium [6]. The chelating carboxylate side-chain provided an opportunity to investigate the impact of increasing the net charge on a transition metal complex without changing the oxidation state or coordination environment of the metal by methylating at oxygen. Ligand methylation has been previously demonstrated to be a viable method to increase the net charge of Ru–NHC complexes [7].

Our strategy was therefore to prepare octahedral ruthenium complexes $[\text{RuL}_n(\text{NHC})]^{m+}$ (**A**) comprising one or more benzimidazolylidene-carboxylate ligands (Figure 1). Coordinative saturation was desired to minimize any variation in electron density at the metal due to changes in coordination number or ligand substitution. Conversion of **A** to $[\text{RuL}_n(\text{NHC-Me})]^{(m+1)+}$ (**B**) via methylation was expected to transform the L,X-type NHC-carboxylate into an L₂-type chelating NHC-ester. Although this reaction at the ligand would be accompanied a +1 increase in net charge for the complex, the formal oxidation state of Ru in **B** would not change. Spectroscopic, crystallographic and electrochemical analysis and comparison of complexes **A** and **B** would then elucidate the impact of increasing the net charge on a complex separately from any increase in oxidation state of the metal center.

Figure 1. Rationale for ligand methylation studies. Methylation of $[\text{RuL}_n(\text{NHC})]^{m+}$ (**A**) will afford $[\text{RuL}_n(\text{NHC-Me})]^{(m+1)+}$ (**B**), with a +1 increase in net charge but no change in Ru oxidation state.

2. Experimental

2.1. Materials and methods

Complex **1**, **3** and $[\text{RuCl}_2(\text{bpy})(\text{dmsO})_2]$ were prepared as previously described [6, 8]. All other materials and solvents were of reagent quality and used as received. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded using a Bruker 500 MHz spectrometer. Chemical shifts δ (in ppm) for ^1H and ^{13}C NMR are referenced to SiMe_4 using the residual protio-solvent as an internal standard [9]. For ^1H NMR: CDCl_3 ,

7.26 ppm; acetone- d_6 , 2.05 ppm. For ^{13}C NMR: CDCl_3 , 77.16 ppm. Coupling constants (J) are expressed in hertz (Hz). Infrared spectra were recorded with 4 cm^{-1} resolution on a Shimadzu IRAffinity-1S spectrometer equipped with a Pike Technologies MIRacle ATR sampling accessory (diamond crystal). Elemental analyses were performed at Atlantic Microlab, Inc. (Norcross, GA). All reactions were performed under an inert atmosphere were performed under an N_2 atmosphere using standard Schlenk or glovebox techniques with the exclusion of light. All workups and purifications were performed under ambient conditions using standard benchtop techniques without requiring exclusion of light. When required, solvents were dried and deoxygenated using an Innovative Technologies solvent purification system, and then stored over molecular sieves (3 Å) in a drybox.

2.2. General spectroscopic considerations

UV–visible absorption spectra were acquired on a Varian Cary 50 Bio spectrometer equipped with a Quantum Northwest TC-125 temperature controller. Room temperature solutions measurements were performed in matched gas-tight quartz cuvettes (Precision Scientific) with 1 cm path lengths and 3.0 mL analyte solution volumes thermostatted at 25 °C. Absorption spectra were acquired in CH_2Cl_2 under an N_2 atmosphere for all analytes. Extinction coefficients (ϵ) were calculated from Beer's law measurements using 10, 20, 30 and 40 μM analyte concentrations.

2.3. Electrochemistry

Electrochemical experiments were conducted on CH Instruments Electrochemical Workstations (series 660D) using a gastight, three-electrode cell under an atmosphere of dry nitrogen. The cell was equipped with gold working and tungsten counter electrodes, as well as a silver wire quasi-reference electrode. Unless specified otherwise, measurements were performed using 1.0 mM solutions of analyte in dry CH_2Cl_2 with 0.10 M [tetra-*n*-butyl-ammonium][PF_6] as the electrolyte and 1.0 mM ferrocene (Fc)

as the internal standard. All potentials reported were determined by cyclic voltammetry at 100 mV s⁻¹ scan rates and referenced to ferrocene by shifting (Fc)^{0/+} to 0.00 V (CH₂Cl₂).

2.4. X-ray crystallographic studies

Single crystals of **2** and **4** were immersed in Paratone-N oil at room temperature and mounted on glass fibers using epoxy glue. The samples were then mounted on the goniometer for data collection at 200 K under a stream of cold nitrogen. Intensity data were collected using Mo K α radiation (λ = 0.71073 Å) and a Mercury CCD detector with a Rigaku AFC8S diffractometer controlled using the CrystalClear software package [10]. The crystal-to-detector distance was 27 mm. Data were collected using ω -scans (0.5° oscillations) using 65 s exposures for **2** and 20 s exposures for **4**. Data were corrected for absorption, Lorentz, and polarization effects using the REQAB subroutine of CrystalClear [11]. The structures were solved by direct methods and subsequently refined using the SHELXTL software package [12]. Further evaluation for higher symmetry and solvent occupancy was done using the PLATON program suite [13]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions using a riding model and assigned thermal parameters equal to either 1.5 (methyl hydrogen atoms) or 1.2 (non-methyl hydrogen atoms) times the thermal parameters of the atoms to which they were attached. For **2**, the ethanol and water solvent molecules were identified from the difference map and modeled by the judicious use of restraints. For **4**, several partially-occupied acetone solvent molecules could initially be identified from the difference map, but their refinement proved problematic, even when heavily restrained. These disordered solvent molecules were instead modeled using the SQUEEZE tool of PLATON (see footnote, Table S1). Crystal data, intensity collection and refinement parameters for **2** and **4** are summarized in the Supporting Information (Tables S1).

2.5. Syntheses

2.5.1. Synthesis of *trans*(C)-[Ru(**1**)₂(bpy)] (**2**)

Complex **1** (323 mg, 0.83 mmol) was dissolved in CHCl₃ (10 mL) and to this solution was added dropwise a solution of [RuCl₂(bpy)(dmsO)₂] (200 mg, 0.41 mmol, 0.5 equiv.) in CHCl₃ (10 mL) and the mixture was then heated to reflux. After 24 h, the reaction mixture was allowed to cool to room temperature and was then filtered through a 0.2 µm PTFE filter (to remove AgCl) with the aid of CHCl₃ (4 mL). The filtrate solvent was removed under reduced pressure and the resulting solids were then dissolved in minimum CH₂Cl₂ and added to 10 mL of hexanes resulting in the formation of a precipitate. The solids were collected via centrifugation, washed with Et₂O (3 × 10 mL) and MeOH (3 × 10 mL), and then dried in vacuo to afford 262 mg (0.32 mmol, 78% yield) of the desired product as a dark red-purple solid. ¹H NMR (500 MHz, CDCl₃): δ = 8.98 (d, *J* = 5.5, 2H), 7.37 (d, *J* = 8.5, 2H), 7.26-7.24 (m, 2H), 7.18 (t, *J*₁ = 8.0, *J*₂ = 15.5, 2H), 6.99 – 6.92 (m, 4H), 6.76 (d, *J* = 8.0, 2H), 6.70 (s, 2H), 6.28 (d, *J* = 8.0, 2H), 6.17 (s, 2H), 5.44 (s, 2H), 5.28 (d, *J* = 16.0, 2H), 5.08 (d, *J* = 15.5, 2H), 1.99 (s, 6H), 1.90 (s, 6H). ¹³C NMR (125 MHz, CDCl₃): δ 198.3, 174.7, 160.0, 152.2, 138.9, 137.6, 137.4, 136.7, 134.6, 130.2, 129.2, 126.1, 125.4, 122.9, 122.8, 122.3, 120.8, 109.7, 109.2, 50.5, 21.2, 21.2. FT-IR (ATR, diamond): UV-vis (CH₂Cl₂), λ (ε) in nm (M⁻¹ cm⁻¹): 293 (sh, 2.05 × 10⁴), 302 (2.59 × 10⁴), 386 (3.57 × 10⁴), 499 (4.07 × 10³), 530 (5.46 × 10³). Anal. Calc. for C₄₄H₃₉N₆O_{4.5}Ru (2·0.5H₂O): C, 64.07; H, 4.77; N, 10.19. Found: C, 63.94; H, 4.84; N, 10.18.

2.5.2. Synthesis of [Ru(**1**)(bpy)₂][OTf] (**4**)

Complex **3** (100 mg, 0.18 mmol) and 2,2'-bipyridine (57 mg, 0.36 mmol, 2.0 equiv.) were dissolved in DMSO (1.5 mL) and stirred at room temperature for 5 min. To this solution was added dropwise a solution of AgOTf (49 mg, 0.19 mmol, 1.1 equiv.) in DMSO (1.5 mL) and the reaction

mixture was heated to 170 °C. After 24 h, the reaction mixture was allowed to cool to room temperature and then added to 10 mL of Et₂O resulting in the formation of a precipitate. The solids were collected via centrifugation, washed with Et₂O (3 × 5 mL), and then purified via column chromatography (Al₂O₃, 99:1 CH₂Cl₂/MeOH, *R_f* = 0.4) to afford 130 mg (0.15 mmol, 83% yield) of the desired product as a dark red-purple solid. ¹H NMR (500 MHz, CDCl₃): δ = 8.95 (d, *J* = 9.5, 1H), 8.88 (d, *J* = 8.0, 1H), 8.36 (d, *J* = 8.0, 1H), 8.29 (d, *J* = 8.0, 1H), 8.23 (d, *J* = 8.0, 1H), 8.09 (td, *J*₁ = 8.0, *J*₂ = 1.3, 1H), 8.03 (td, *J*₁ = 7.9, *J*₂ = 1.2, 1H), 7.87 (d, *J* = 8.5, 1H), 7.79 (td, *J*₁ = 7.9, *J*₂ = 1.2, 1H), 7.63 (td, *J*₁ = 6.8, *J*₂ = 1.0, 1H), 7.54–7.45 (m, 3H), 7.40 (d, *J* = 8.0, 1H), 7.29 (td, *J*₁ = 7.8, *J*₂ = 0.7, 1H), 7.16 (td, *J*₁ = 6.5, *J*₂ = 1.0, 1H), 7.12 (t, *J* = 7.8, 1H), 7.04 (dd, *J*₁ = 5.5, *J*₂ = 0.5, 1H), 7.00 (td, *J*₁ = 6.6, *J*₂ = 1.3, 1H), 6.79 (s, 1H), 6.53 (d, *J* = 8.0, 1H), 6.37 (s, 1H), 5.54 (s, 1H), 5.08 (d, *J* = 16.5, 1H), 4.57 (d, *J* = 16.5, 1H), 2.03 (s, 3H), 1.91 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 197.8, 172.5, 158.9, 158.1, 157.6, 155.6, 154.5, 151.6, 150.8, 148.8, 139.7, 138.7, 138.1, 137.5, 136.9, 136.3, 135.9, 134.9, 134.6, 131.4, 127.7, 126.8, 126.5, 125.7, 125.6, 124.8, 124.1, 123.9, 123.5, 123.4, 123.3, 122.8, 110.4, 108.8, 50.8, 21.3, 21.1. UV–vis (CH₂Cl₂), λ (ε) in nm (M^{−1} cm^{−1}): 290 (sh, 1.49 × 10⁵), 296 (1.68 × 10⁵), 360 (4.92 × 10⁴), 460 (sh, 2.43 × 10⁴), 496 (2.93 × 10⁴). Anal. Calc. for C₃₈H₃₁F₃N₆O₅S₁Ru (4·H₂O): C, 53.08; H, 3.87; N, 9.77. Found: C, 53.14; H, 3.99; N, 9.75.

2.5.3. Synthesis of *trans*(C)-[Ru(**1-Me**)₂(bpy)][OTf]₂ (**5**)

Complex **2** (50 mg, 61 μmol) was dissolved in CH₂Cl₂ (2 mL) and then cooled to −30 °C. After 30 min, 0.20 mL of a 0.77 M solution of MeOTf in CH₂Cl₂ (0.15 mmol, 2.5 equiv.) was added dropwise and the reaction was allowed to warm to room temperature and stirred for 2h. The solution was then concentrated to 1 mL and added to 10 mL of hexanes resulting in the formation of a precipitate. The solids were collected via centrifugation, washed with EtOAc (3 × 5 mL) and Et₂O (3 × 5 mL), and then dried in vacuo to afford 65 mg (57 μmol, 93% yield) of the desired product as a light orange-red solid.

^1H NMR (500 MHz, acetone- d_6): δ = 8.58 (d, J = 5.5, 2H), 7.88–7.80 (m, 4H), 7.78 (t, J = 7.8, 4H), 7.37 (t, J = 7.8, 2H), 7.19 (t, J = 7.5, 2H), 7.15 (t, J = 5.8, 2H), 6.94 (s, 2H), 6.77 (s, 2H), 6.56 (d, J = 8.0, 2H), 5.80 (d, J = 4.5, 4H), 5.72 (s, 2H), 4.27 (s, 6H), 2.13 (s, 6H), 2.05 (s, 6H, overlaps acetone- d_5). UV–vis (CH_2Cl_2), λ (ϵ) in nm ($\text{M}^{-1} \text{cm}^{-1}$): 296 (8.59×10^4), 329 (5.06×10^4), 445 (1.10×10^4). Anal. Calc. for $\text{C}_{48}\text{H}_{45}\text{F}_6\text{N}_6\text{O}_{10.5}\text{S}_2\text{Ru}$ (**5**·0.5 H_2O): C, 50.00; H, 3.93; N, 7.29. Found: C, 49.91; H, 3.94; N, 7.20.

2.5.4. Synthesis of $\text{Ru}(\textbf{I-Me})(\text{bpy})_2][\text{OTf}]_2$ (**6**)

Complex **4** (50 mg, 59 μmol) was dissolved in CH_2Cl_2 (2 mL) and then cooled to -30°C . After 30 min, 0.10 mL of a 0.77 M solution of MeOTf in CH_2Cl_2 (77 μmol , 1.3 equiv.) was added dropwise and the reaction was allowed to warm to room temperature and stirred for 2h. The solution was then concentrated to 1 mL and added to 10 mL of hexanes resulting in the formation of a precipitate. The solids were collected via centrifugation, washed with Et_2O ($3 \times 5 \text{ mL}$), and then dried in vacuo to afford 57 mg (57 μmol , 97% yield) of the desired product as a light orange-red solid. ^1H NMR (500 MHz, acetone- d_6): δ = 9.52 (d, J = 5.0, 1H), 8.93 (d, J = 5.0, 1H), 8.79 (d, J = 8.3, 1H), 8.71 (d, J = 8.3, 1H), 8.57 (d, J = 8.2, 1H), 8.35 (t, J = 7.4, 1H), 8.28 (t, J = 7.4, 1H), 8.18–8.10 (m, 2H), 7.88 (d, J = 8.3, 1H), 7.80–7.75 (m, 2H), 7.74–7.68 (m, 2H), 7.59–7.51 (m, 2H), 7.39 (t, J = 7.6, 1H), 7.25–7.17 (m, 2H), 6.87 (s, 1H), 6.68 (s, 1H), 6.59 (d, J = 8.3, 1H), 5.85 (d, J = 18.3, 1H), 5.69 (s, 1H), 5.44 (d, J = 18.4, 1H), 3.81 (s, 3H), 2.07 (s, 3H), 1.86 (s, 3H). UV–vis (CH_2Cl_2), λ (ϵ) in nm ($\text{M}^{-1} \text{cm}^{-1}$): 291 (1.43×10^5), 330 (6.28×10^4), 429 (2.03×10^4), 454 (2.30×10^4). Anal. Calc. for $\text{C}_{40}\text{H}_{34}\text{F}_6\text{N}_6\text{O}_8\text{S}_2\text{Ru}$: C, 47.76; H, 3.41; N, 8.35. Found: C, 47.32; H, 3.77; N, 7.96.

3. Results and discussion

3.1. Synthesis and characterization

Each benzimidazolylidene-carboxylate ligand will occupy two coordination sites, thus any Ru-containing starting material must have two (or a multiple of two) vacant coordination sites or easily-displaceable ligands. Furthermore, coordinative saturation at Ru and resistance of the methylated product to substitution reactions can be achieved with an octahedral geometry and chelating ligands, respectively. Based on these considerations, we sought to incorporate the benzimidazolylidene-carboxylate ligand into Ru complexes bearing one or two bpy ligands (bpy = 2,2'-bipyridyl).

Silver-NHC complexes are useful for the synthesis of other transition metal-NHC complexes because they supply an NHC without requiring the synthesis and isolation of the free carbene [14]. Complex [Ag(**1**)] is particularly versatile because it can abstract a halide from as well as transfer its NHC to another transition metal center. We have previously reported that the NHC in [Ag(**1**)], a carboxylate-functionalized benzimidazolylidene, can function as a bidentate L,X type ligand for Ru [6].

The complex [RuCl₂(bpy)(dms_o)₂] has been used to prepare coordinately-saturated octahedral Ru complexes [8] and, upon reaction with 2 equiv. of [Ag(**1**)], afforded the desired Ru–NHC complex *trans*(C)-[Ru(**1**)₂(bpy)] (**2**), featuring two carboxylates available for methylation (reaction *a*, Scheme 1). ¹H NMR spectroscopic analysis revealed that both NHC ligands in **2** were equivalent, presumably due to the C₂ axis bisecting N–Ru–N. Additionally, the signal for the N–CH₂ protons shifted from the singlet at 5.17 ppm in [Ag(**1**)] to two doublets at 5.28 and 5.08 ppm in **2**, indicating the protons had become inequivalent (i.e. two protons were oriented towards the bpy ligand and two away from it). The fact that the N–CH₂ protons became diastereotopic was diagnostic for the formation of a C–Ru–O chelate ring, and has previously been observed with **3**. Remarkably, one of the 3,5-dimethylphenyl aromatic proton signals in **2** was observed at 5.04 ppm, significantly upfield of any of the corresponding signals in [Ag(**1**)] (7.21 and 7.10 ppm).

Scheme 1. Synthesis of **2** and **4**. Reagents and conditions: (a) 0.5 equiv. $[\text{RuCl}_2(\text{bpy})(\text{dmsO})_2]$, CHCl_3 , reflux, 24 h, 78% yield; (b) 0.5 equiv. $[\text{RuCl}(\eta^6\text{-cymene})(\mu\text{-Cl})_2]$, CH_2Cl_2 , RT, 24 h, 97% yield; (c) 2 equiv. 2,2'-bipyridine, 1.05 equiv. AgOTf , DMSO, 170°C , 24 h, 83% yield. $\text{OTf} = \text{O}_3\text{SCF}_3$, $\text{R} = 3,5\text{-dimethylphenyl}$.

Having prepared a complex that could increase in net charge by +2, we next sought to prepare a complex that could increase in net charge by +1. Because complex **2** had the formula $[\text{Ru}(\textbf{1})_2(\text{bpy})]$, we reasoned that a suitable target would have the formula $[\text{Ru}(\textbf{1})(\text{bpy})_2][\text{A}]$ ($\text{A} = \text{non-coordinating anion}$). Initial efforts were directed towards the reaction of **[Ag(1)]** with *cis*- $[\text{RuCl}_2(\text{bpy})_2]$ [15], in conjunction with a variety of halide abstracting reagents, but only complicated mixtures were obtained, containing trace amounts of the desired product along with starting materials, intermediate byproducts, and ligand decomposition products. Given that installing the NHC onto a $[\text{Ru}(\text{bpy})_2]$ complex was unsuccessful, an alternate route was pursued in which two bpy ligands would be installed onto a pre-formed $[\text{Ru}(\text{NHC})]$ complex [16]. Reaction of complex **3** with 2 equiv. of bpy in the presence of AgOTf afforded $[\text{Ru}(\textbf{1})(\text{bpy})_2][\text{OTf}]$ (**4**) in good yield (reaction c, Scheme 1).

No C_2 symmetry was present in complex **4** and its ^1H NMR spectrum revealed all the protons in

bpy ligands were inequivalent. Whereas **4** had a +1 net charge and **2** was overall neutral, the ^1H NMR spectroscopic data indicated no straightforward trend that the ligands in **4** were significantly more electron deficient, and therefore more deshielded, than those in **2**. Similar to **2**, the N-CH₂ protons in **4** were diastereotopic, but the doublets in **4** (5.08 and 4.57 ppm) were located upfield of the corresponding signals in **2**. Conversely, the 3,5-dimethylphenyl aromatic protons in **4** (6.79, 6.37 and 5.54 ppm) resonated slightly downfield of those in **2** (6.70, 6.17 and 5.44 ppm). Furthermore, the most downfield bpy ^1H NMR signals occurred at nearly identical chemical shifts (8.95 ppm for **4** vs. 8.98 ppm for **2**). Although no trend was discernible from the individual proton resonances, the aromatic protons in **4** were collectively more downfield than those in **2**. Of the 23 aromatic protons in complex **4**, 15 were located downfield of the residual CHCl₃ peak, compared to only 4 of the 22 aromatic protons in complex **2**.

Reaction of **2** with 2.5 equiv. of MeOTf afforded the dimethylated complex *trans*(C)-[Ru(**1-Me**)₂(bpy)][OTf]₂ (**5**) in excellent yield (93%, reaction *a*, Scheme 2). Similar to complex **2**, the ^1H NMR spectrum of **5** revealed that the NHC ligands were equivalent. Methylation of the carboxylate moiety of the NHC ligand was inferred from the presence of a peak at 4.27 ppm and relative integration of 6, consistent with the formation of two methyl ester functional groups. In addition, the N-CH₂ signal shifted significantly downfield to 5.80 ppm (vs. 5.28 ppm in **2**) and 10 of the 22 aromatic protons were downfield of 7.26 ppm (vs. 4 protons in **2**).

Scheme 2. Synthesis of **5** and **6**. Reagents and conditions: (a) 2.5 equiv. MeOTf, CH₂Cl₂, −30 °C → RT, 2 h, 93% yield. (b) 1.3 equiv. MeOTf, CH₂Cl₂, −30 °C → RT, 2 h, 97% yield. OTf = O₃SCF₃, R = 3,5-dimethylphenyl.

Similarly, reaction of complex **4** with 1.3 equiv of MeOTf afforded monomethylated complex [Ru(**1-Me**)(bpy)₂][OTf]₂ (**6**) in near-quantitative yield (97%, reaction *b*, Scheme 2). A new singlet at 3.81 ppm was present in the ¹H NMR spectrum of **6** that was attributed to the formation of a methyl ester. Additionally, the doublets for the N-CH₂ protons in **6** (5.85 and 5.44 ppm) were significantly downfield of the corresponding peaks in the ¹H NMR spectrum of **4** (5.08 and 4.57 ppm), consistent with a +1 increase in net charge on the complex rendering the metal (and thus also the ligands attached to it) more electron deficient. In support of this conclusion, the most downfield peak in the ¹H NMR spectrum of **6** was at 9.52 ppm, compared to 8.95 ppm for **4**.

All attempts to isolate the monomethylated analog of **5**, comprising one methyl ester and one carboxylate, were unsuccessful. Reaction of **2** with 0.1 equiv. of MeOTf at −78 °C, quenching via precipitation at this temperature, and immediate ¹H NMR analysis of the crude precipitate revealed one additional methyl ester peak (4.20 ppm) and four aryl-CH₃ (2.18, 2.07, 1.95 and 1.93 ppm) singlets

distinct from the resonances arising from **2** or **5**. Despite the low temperature and low stoichiometry employed in this reaction, complex **5** was also observed in this ¹H NMR spectrum in a 1:2 ratio with the supposed monomethylated complex. Unfortunately, all complexes isolated from the reactions of **2** or **4** with MeOTf, including analytically-pure samples of **5** and **6**, were unstable in solution (e.g. CDCl₃, CD₂Cl₂, THF-*d*₈, acetone-*d*₆), which precluded more detailed NMR spectroscopic analysis.

3.2. Coordination chemistry

Single crystals of **2** suitable for X-ray diffraction were grown via diffusion of Et₂O vapor into a solution of **2** in EtOH at room temperature. Crystallographic analysis revealed the two NHC moieties in **2** were oriented *trans* relative to each other (Figure 2), a configuration that minimized negative steric interactions between the two N-aryl substituents. Overall, the metric parameters determined for **2** were consistent with similar complexes that have been previously reported. More specifically, the Ru–C distances (2.057(7) and 2.062(7) Å) and the Ru–O distances (2.111(5) and 2.113(4) Å) in **2** fell within the range of values observed for comparable Ru–NHC (2.003–2.089 Å) [17] and Ru–carboxylate (2.065–2.115 Å) [18] complexes. Interestingly, the average C–O bond distances to the terminal oxygen (1.255(9) Å) and the oxygen coordinated to Ru (1.260(9) Å) were nearly identical in **2**, suggesting a significant degree of charge delocalization within the carboxylate moieties.

Figure 2. ORTEP diagram rendered using the POV-Ray engine, shown with 50% probability thermal ellipsoids and selected atom labels for **2**. Hydrogen atoms, solvent molecules and N-aryl substituents have been omitted for clarity. Selected distances (Å) and angles (°): Ru1–O1, 2.111(5); Ru1–O3, 2.113(4); Ru1–N5, 2.008(5); Ru1–N6, 2.021(5); Ru1–C1, 2.057(7); Ru1–C18, 2.062(7); O1–Ru1–O3, 90.48(19); N5–Ru1–N6, 80.3(2); O1–Ru1–C1, 84.6(2); O3–Ru1–C18, 85.8(2); C1–Ru1–C18, 166.1(3).

Figure 3. ORTEP diagram rendered using the POV-Ray engine, shown with 50% probability thermal ellipsoids and selected atom labels for **5**. Hydrogen atoms, solvent molecules, counterions and N-aryl substituents have been omitted for clarity. Selected distances (Å) and angles (°): Ru1–O1, 2.139(5); Ru1–O3, 2.141(4); Ru1–N5, 2.011(5); Ru1–N6, 2.017(5); Ru1–C1, 2.089(6); Ru1–C19, 2.052(6); O1–Ru1–O3, 86.47(18); N5–Ru1–N6, 79.2(2); O1–Ru1–C1, 86.4(2); O3–Ru1–C19, 85.3(2); C1–Ru1–C19,

171.6(2).

Methylation of the terminal carboxylate oxygen atoms upon reaction of **2** with MeOTf, inferred by the presence of a methyl ester OCH₃ peak in the ¹H NMR spectrum of **5**, was confirmed by crystallographic analysis (Figure 3). Although **5** had a +2 net charge and **2** was overall neutral, the Ru–C distances (2.052(6) and 2.089(6) Å) and the Ru–N distances (2.011(5) and 2.017(5) Å) in **5** were not significantly different from those in **2**. Methylation of the ligand in **2** should convert the charge-delocalized carboxylate moieties to neutral esters that bind Ru via their carbonyl oxygen atoms. The average C–O bond distance to the methylated oxygen (1.317(8) Å) was substantially greater than to the Ru-bound oxygen (1.221(8) Å) in **5**, consistent with significant differentiation into single- and double-bond character, respectively. The Ru–O distances (2.139(5) and 2.141(4) Å) in **5** were only 2.8 picometers longer than the corresponding distances in **2**, despite the fact that **5** featured a Ru bound to the carbonyl oxygen of a neutral ester ligand, whereas **2** featured a Ru bound to the carboxylate oxygen of an anionic carboxylate ligand. Compared to **2**, the C–Ru–C angle in **5** (171.6(2)°) was slightly more obtuse and the O–Ru–O angle (86.47(18)°) was slightly more acute, which could be due to steric repulsion between the two OMe moieties in **5**.

3.2. Electrochemistry

Cyclic voltammetry of **2** revealed a quasireversible peak at –0.14 V (vs. Fc) that was attributed to the Ru(II)/Ru(III) redox couple (black line, Figure 4A). Similar analysis of **5** indicated that the analogous oxidation process occurred at a potential 0.81 V higher in **5** ($E_{1/2}$ = 0.67 V, grey line, Figure 4A) than in **2**, despite the fact that both **2** and **5** comprised Ru centers in the same oxidation state coordinated to ligand atoms with nearly identical bond distances. Presumably, the +2 net charge in **5** that formally resided on Ru significantly lowered the energy of the metal-centered orbitals and, in doing so,

raised the energy required to remove electrons from them.

Figure 4. Cyclic voltammograms of (A) **2** (black line) and **5** (grey line) and (B) **4** (black line) and **6** (grey line) in CH₂Cl₂ containing 1.0 mM analyte and 0.10 M [Bu₄N][PF₆] at 100 mV s⁻¹ scan-rate.

Complex **4** exhibited a Ru(II)/Ru(III) redox couple at 0.45 V (black line, Figure 4B), a potential significantly higher than the corresponding value in **2**, which could be attributed to **4** having a +1 net charge and **2** being overall neutral. Unlike **2**, however, complex **4** also exhibited a quasireversible reduction at -1.95 V (Figure S1). The oxidation potential measured for **6** ($E_{1/2} = 0.82$ V, grey line, Figure 4B) was higher than in **4**, but the difference between the Ru(II)/Ru(III) oxidation potential in **4** and **6** ($\Delta E_{4 \rightarrow 6} = 0.37$ V) was substantially lower than between **2** and **5** ($\Delta E_{2 \rightarrow 5} = 0.81$ V). Similar to **4**, complex **6** displayed reduction peaks, albeit irreversible ones, at -1.02 and -1.81 V (Figure S2). Unfortunately, both **5** and **6** decomposed under all cyclic voltammetry experimental conditions after 2-3

scans, which precluded more detailed analyses.

The increase in Ru(II)/Ru(III) oxidation potential showed a linear correlation with the increase in the net charge on the complex. More specifically, the increase in oxidation potential going from **2** to **5** was 2.2 times greater than the increase from **4** to **6** (0.81 V / 0.37 V), and the increase in net charge from **2** to **5** was twice that from **4** to **6**. Examination of the oxidation onset potentials, instead of the half-wave potentials, revealed a closer correlation with net charge. The onset for the Ru(II)/Ru(III) oxidation in **5** occurred at a potential 0.77 V higher in energy than in **2** (0.58 vs. -0.19 V, respectively), and the corresponding process in **6** was 0.38 V higher than in **4** (0.73 vs. 0.35 V, respectively). Therefore, the increase in oxidation onset potential going from **2** to **5** was twice the increase from **4** to **6** (0.77 V / 0.38 V).

3.2. Spectroscopy

The Ru-NHC complexes were then analyzed by UV-visible spectroscopy to elucidate any correlation between net charge and optical properties. Because the electrochemistry experiments revealed the Ru(II)/Ru(III) oxidation potentials were strongly affected by net charge, the lowest-energy optical transitions were examined, given that they likely involved transitions to or from metal-centered orbitals. The longest-wavelength peaks in **2** and **5** occurred at 530 nm (2.34 eV) and 445 nm (2.79 eV), respectively (Figure 5A). Similar analysis of **4** and **6** revealed their longest-wavelength peaks occurred at 496 nm (2.50 eV) and 454 nm (2.73 eV), respectively (Figure 5B). The difference in longest-wavelength optical transition energy (ΔE_{opt}) between **5** and **2** was 0.45 eV, whereas ΔE_{opt} was 0.23 eV between **6** and **4**. Considering the ratio of these ΔE_{opt} values, the increase in energy going from **2** to **5** was double the increase from **4** to **6** (0.45 eV / 0.23 eV).

Figure 5. Cyclic voltammograms of (A) **2** (black line) and **5** (grey line) and (B) **4** (black line) and **6** (grey line) in CH_2Cl_2 containing 1.0 mM analyte and 0.10 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ at 100 mV s^{-1} scan-rate.

A similar trend was observed with the second-lowest energy peaks. After the transition at 530 nm, the next longest wavelength peak for **2** was located at 386 nm (3.21 eV). Conversion to **5** shifted this peak to 329 nm (3.77 eV), a 0.56 eV increase in energy. Analogous peaks in **4** and **6** were observed at 360 nm (3.44 eV) and 330 nm (3.75 eV), respectively, corresponding to an energy difference of 0.31 eV. Based on this second set of peaks, the increase in energy going from **2** to **5** was 1.8 times the increase from **4** to **6** (0.56 eV / 0.31 eV). Although the ratios determined from UV/vis spectroscopy were in good agreement with those obtained via electrochemistry, the possibility that the similarity of these ratio values was coincidental could not be definitively excluded. The UV/vis spectra of **2**, **4**, **5** and **6** all displayed multiple transitions, some overlapping, which complicated peak assignments and consequently any interpretation of shifts in energy due to changes in net charge.

4. Conclusions

A chelating benzimidazolylidene-carboxylate ligand was used to prepare the complexes *trans*(C)-[Ru(**1**)₂(bpy)] (**2**) and [Ru(**1**)(bpy)₂][OTf] (**4**). With two NHC-carboxylate ligands, the net charge on **2** was increased by +2 upon methylation to give *trans*(C)-[Ru(**1-Me**)₂(bpy)][OTf]₂ (**5**). Similarly, the one NHC-carboxylate ligand in **4** reacted with MeOTf to afford [Ru(**1-Me**)(bpy)₂][OTf]₂ (**6**), accompanied by a +1 increase in net charge. Cyclic voltammetry revealed the increase in Ru(II)/Ru(III) oxidation half-wave and onset potentials was 2.2 and 2.0 times greater, respectively, when accompanied by a +2 increase in net charge vs. a +1 increase. UV–visible spectroscopic analysis suggested the first and second longest-wavelength peaks in **2** were shifted to higher energy in **5** by a factor of 2.0 and 1.8, respectively, greater than the corresponding shift from **4** to **6**. Despite these substantial changes in oxidation potentials and absorption wavelengths, the X-ray crystal structures of **2** and **5** showed that there were no significant changes in metal–ligand bond distances.

Collectively, these results demonstrate that the Ru centers in **5** and **6** were rendered more electron deficient than those in **2** and **4**, respectively, by amounts linearly proportional to the increase in the net charge of the complexes. Furthermore, the high degree of similarity of the metric parameters in **2** and **5** suggested that the changes in electron density at the metal centers observed by electrochemistry and UV/vis spectroscopy were not caused by significant changes in coordination chemistry. Because [Ag(**1**)] can install the benzimidazolylidene-carboxylate ligand onto a variety of transition metal complexes and methylation of the carboxylate moiety with MeOTf can increase net charge without changing the formal oxidation state or coordination chemistry of the metal center, this represents a general strategy for studying the effects of net charge on the electronic and optical properties of organotransition metal complexes.

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Appendix A. Supplementary material

Supplementary data associated with this article (Cyclic voltammograms; crystallographic data tables; ^1H and ^{13}C NMR spectra; CIF files) can be found, in the online version, at <http://dx.doi.org/10.1016/j.ica.XXXX>.

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$[\text{Ru}(\text{L-L})_2(\text{bpy})]^{2+}$

$[\text{Ru}(\text{L-X})_2(\text{bpy})]$