

Synthetic Strategies for Trapping the Elusive *trans*-Rh₂(II,II) Formamidinate Isomer: Effects of *Cis* versus *Trans* Geometry on the Photophysical Properties

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ABSTRACT: The *cis* and *trans* dirhodium(II,II) complexes *cis*-[Rh₂(μ-DTolF)₂(μ-np)(MeCN)₄][BF₄]₂ (**1**, DTolF = N,N'-di(*p*-tolyl)formamidinate; np = 1,8-naphthyridine), *cis*- and *trans*-[Rh₂(μ-DTolF)₂(μ-qxnp)(MeCN)₃][BF₄]₂ (**2** and **3**, respectively, where qxnp = 2-(1,8-naphthyridin-2-yl)quinoxaline), and *trans*-[Rh₂(μ-DTolF)₂(μ-qxnp)₂][BF₄]₂ (**4**), were synthesized and characterized. A new synthetic methodology was developed that consists of the sequential addition of π-accepting axially-blocking ligands to favor the formation of the first example of a bis-substituted formamidinate-bearing *trans* product. Isolation of the intermediates **2** and **3** provides insight into the mechanistic requirements for obtaining **4** and the *cis* analog, *cis*-[Rh₂(μ-DTolF)₂(μ-qxnp)₂][BF₄]₂ (**5**). Density functional theory (DFT) calculations provide support for the synthetic mechanism and proposed intermediates. The metal/ligand-to-ligand charge transfer (ML-LCT) absorption maximum of the *trans* complex **4** at 832 nm is red-shifted by 1173 cm⁻¹ and exhibits shorter lifetimes of the ¹ML-LCT and ³ML-LCT excited states, 3 ps and 0.40 ns, respectively, as compared to the *cis* analog, **5**. The shorter excited state lifetimes of **4** are attributed to the longer Rh-Rh bond of 2.4942(8) Å, relative to that in **5**, 2.4498(2) Å. A longer metal-metal bond reflects a decreased overlap of the rhodium atoms that leads to more accessible metal-centered excited state for radiationless deactivation. The ³ML-LCT excited states of **4** and **5** undergo reversible bimolecular charge transfer with the electron donor *p*-phenylenediamine when irradiated with low-energy light. These results indicate that *trans* isomers are a source of unexplored tunability for potential p-type semiconductor applications and, given their distinct geometric arrangement, constitute useful building blocks for supramolecular architectures with potentially interesting photophysical properties.

INTRODUCTION

The increasing demand for energy requires more efficient carbon-free renewable energy sources.¹ Solar energy conversion has proven to be an environmentally friendly method for producing electricity and clean fuels, such as hydrogen.²⁻⁶ The use of dye-sensitized solar cells (DSSCs) is attractive due to the relatively low cost of fabrication, high tunability, flexibility, and durability.⁷⁻¹¹ While DSSCs have theoretical efficiencies of 35% and 43% in the case of n-type and tandem (n-type and p-type) sensitized solar cells,¹²⁻¹⁴ respectively, the highest efficiency measured thus far in commercial devices is ~11.9%.^{15, 16} Ideally, DSSC photosensitizers should exhibit a panchromatic absorption profile in order to efficiently harvest the full solar spectrum, as well as excited state properties that support hole injection even with low energy light excitation.^{10, 11}

There are numerous limitations to the design of efficient sensitizers. The current record is held by the SM315 porphyrin coupled to a Co(II/III) redox shuttle.¹⁷ This system exhibits a 13% photocurrent efficiency (PCE) and displays panchromatic absorption, but the lowest energy electronic transition has a maximum at 668 nm and does not absorb beyond 800 nm. Other types of phthalocyanines and porphyrins have very large absorption coefficients in the near-IR region but aggregate on the surface of the semiconductor which decreases their overall efficiency.¹⁸ The gold standard for n-type sensitized DSSCs, the N3 Ru(II) dye, has an efficiency of 10-12%, in part due to its inability to absorb light beyond 600 nm.^{19, 20} Other promising dyes are BODIPY derivatives,²¹⁻²³ but their very narrow absorption profiles preclude absorption of the full solar spectrum. Given these shortcomings, the design of new panchromatic photosensitizers with good solubility and chemical stability that utilize both high and low

energy light to undergo charge transfer reactions is critical for the development of improved DSSCs.

Recently, our groups reported a series of dirhodium(II,II) complexes that feature electron donating formamidinate bridging ligands and π -accepting bridging ligands with substituents designed to block the axial coordination sites.^{24, 25} These complexes are capable of participating in electron transfer reactions upon irradiation with low-energy light, including the oxidation of *p*-phenylenediamine and reduction of electron acceptors, rendering them suitable for both n-type and p-type semiconductor applications. As the coordination sphere is chemically modified, the excited state redox potential of these partial paddlewheel $\text{Rh}_2(\text{II,II})$ complexes can be tuned such that they are capable of undergoing electron transfer to acceptors and n-type semiconductors.^{24, 25} In this vein, it was discovered that axially-blocked complexes exhibit significantly longer ³ML-LCT lifetimes (7 – 25 ns) compared to those with solvent accessible axial sites, such as *cis*- $[\text{Rh}_2(\mu\text{-DTolF})_2(\mu\text{-np})_2][\text{BF}_4]_2$ (DTolF = N,N'-di(*p*-tolyl)formamidinate; np = 1,8-naphthyridine), with a ³ML-LCT lifetime of ~ 0.5 ns.^{24, 25} The longer lifetimes are necessary for bimolecular electron transfer reactions, but are not required for charge injection into semiconductors, which has been shown to occur within fs to ps.²⁶ In addition, this class of $\text{Rh}_2(\text{II,II})$ complexes was shown to photosensitize the production of H_2 with $\lambda_{\text{irr}} = 655 \text{ nm}$,²⁷ as well as to inject electrons into TiO_2 from its ¹ML-LCT state with 600 nm light,²⁸ both of which represent improvements over the N3 dye.

Bis-substituted *cis*- and *trans*-dirhodium(II,II) complexes have been used extensively as catalysts for organic transformations,^{29, 30} but the excited state properties and photochemistry of these complexes were not investigated. Our groups have studied the excited states and reactivity,^{25, 31, 32} photochemistry,³³ and photoinduced biological activity of *cis*-dirhodium(II,II) complexes,³⁴⁻³⁹ but the photochemistry of the *trans* isomers remains unexplored. The possibility of obtaining the *trans* isomers opens up new opportunities for the exploration of novel supramolecular assemblies with potentially interesting photophysical properties. In this vein, we note that *cis* isomers of dirhodium(II,II) complexes with amidines or triphenylphosphine bridging ligands are interesting but of limited use. These complexes have been used as corner motifs to prepare square and triangular-shaped supramolecular assemblies since the angle between bridging ligands is ~ 90°.^{40, 41} Given that the *trans* isomers display a ~ 180° between bridging ligands, they are much more versatile as building blocks for a wide variety of shapes including ladder structures and numerous polygonal assemblies, including triangles, rectangles, and hexagons, among others.^{42, 43}

The synthesis of heteroleptic dirhodium(II,II) complexes is governed by the kinetic *trans* effect which explains why the vast majority of partial paddlewheel complexes in the literature are bis-substituted with a *cis* configuration.⁴⁴ The substitution chemistry of dirhodium complexes follows the same criteria as the archetypal square planar

complexes *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ and *trans*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. The basicity of a ligand is proportional to the *trans* effect exerted on the ligand opposite to it, which determines the geometric arrangement of the final product. For example, given that CH_3CO_2^- is more basic than CF_3CO_2^- , the complex *cis*- $\text{Rh}_2(\text{CH}_3\text{CO}_2)_2(\text{CF}_3\text{CO}_2)_2$ can be obtained from $\text{Rh}_2(\text{CH}_3\text{CO}_2)_4$ in the presence of two equivalents of $\text{CF}_3\text{CO}_2\text{H}$, while the *trans* analogue can be obtained from the reaction of $\text{Rh}_2(\text{CF}_3\text{CO}_2)_4$ and $\text{CH}_3\text{CO}_2\text{H}$.⁴⁵ Of particular relevance to the current study is the fact that formamidinate ligands have a very strong *trans* effect due to their markedly strong basicity with respect to other bridging ligands such as amidinates and acetates. As a consequence, there are no examples of *trans* formamidinate-containing dirhodium complexes reported in the literature to this date. Other examples of note are the rare *cis/trans* isomeric pairs of $[\text{Rh}_2(\text{OAc})_2(\text{PhTCB})_2]$ (where PhTCB = phenylthiocarbamoyl benzoate) which were isolated as isomeric mixtures and tested as catalysts for cyclopropanation of alkene substrates.⁴⁶ This chemistry, however, did not lead to pure compounds, which prevents correlation between geometry and properties.

Herein we report a new synthetic methodology for the preparation of *trans*- $\text{Rh}_2(\text{II,II})$ isomers containing two DTolF formamidinate ligands namely *cis*- $[\text{Rh}_2(\mu\text{-DTolF})_2(\mu\text{-np})(\text{MeCN})_4][\text{BF}_4]_2$ (**1**, where np = 1,8-naphthyridine), *cis/trans*- $[\text{Rh}_2(\mu\text{-DTolF})_2(\mu\text{-qxnp})(\text{MeCN})_3][\text{BF}_4]_2$ (**2/3** respectively, where qxnp = 2-(1,8-naphthyridin-2-yl)quinoxaline), and *trans*- $[\text{Rh}_2(\mu\text{-DTolF})_2(\mu\text{-qxnp})_2][\text{BF}_4]_2$ (**4**) (Figure 1). The photophysical and electronic properties were measured and compared to those of the previously reported complex **5**, *cis*- $[\text{Rh}_2(\mu\text{-DTolF})_2(\mu\text{-qxnp})_2][\text{BF}_4]_2$. The new compounds display panchromatic absorption spectra from the UV to the near-IR region. The synthetic approach used in these studies represents a new strategy for the preparation of rare dirhodium *trans* derivatives that constitute a new family of bimetallic architectures. These complexes have potentially useful photochemical properties for applications in solar energy conversion and photochemotherapy, as well as for the design and synthesis of new supramolecular assemblies with interesting photophysical properties.

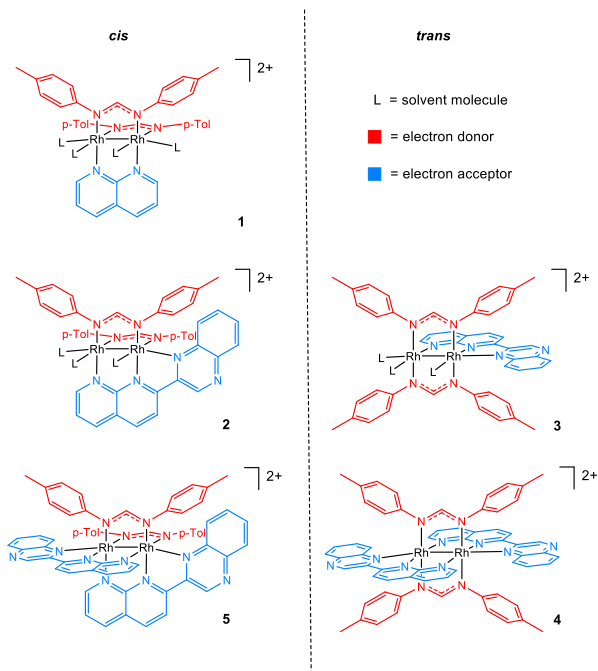


Figure 1. Schematic representations of complexes **1** – **5**.

EXPERIMENTAL SECTION

Materials. The starting material $[\text{RhCl}(\text{COD})]_2$ (COD = 1,5-cyclooctadiene) was purchased from Pressure Chemicals and used without further purification to prepare the partially solvated compound $\text{cis-}[\text{Rh}_2(\mu\text{-DTolF})_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ following a reported procedure.⁴⁷ The 1,8-naphthyridine (np) ligand was purchased from Oakwood Chemicals and used as received. The ligand 2-(1,8-naphthyridin-2-yl)quinoxaline (qxnp) and the protonated form of DTolF, N,N'-di(*p*-tolyl)formamidinium (HDTolF) were synthesized following reported procedures,⁴⁸ using *p*-toluidine purchased from Alfa Aesar and triethyl orthoformate obtained from TCI which were used without further purification. Chlorobenzene was used as received and acetonitrile was dried over 3 Å molecular sieves and distilled under a N_2 atmosphere. The salt $\text{cis-}[\text{Rh}_2(\mu\text{-DTolF})_2(\text{qxnp})_2][\text{BF}_4]_2$ (**5**) was prepared by a reported method.²⁴ All compounds were synthesized under inert atmosphere conditions using Schlenk-line techniques with subsequent manipulation and purification of the complexes being performed in air.

$\text{cis-}[\text{Rh}_2(\mu\text{-DTolF})_2(\mu\text{-np})(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ (**1**). Quantities of $\text{cis-}[\text{Rh}_2(\mu\text{-DTolF})_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ (100.1 mg, 0.093 mmol) and 11.9 mg of np (0.091 mmol) were added to a Schlenk flask and refluxed for 24 h in 20 mL of dry acetonitrile. The dark purple solution was evaporated under vacuum to near dryness and the product was precipitated with diethyl ether. The solution was filtered through a fine frit, and the dark pink solid was washed with diethyl ether. The product was purified by slow diffusion of diethyl ether into a concentrated acetonitrile solution to yield 89.1 mg of compound (85 %). Dark pink X-ray quality crystals were obtained by slow diffusion of diethyl ether into a concentrated solution of the compound in acetonitrile. ^1H NMR (500 MHz, CD_3CN) δ 9.65 (dd, J = 5.2,

1.6 Hz, 2H), 8.59 (dd, J = 8.2, 1.6 Hz, 2H), 7.75 (dd, J = 8.2, 5.2 Hz, 2H), 7.68 (t, J = 3.5 Hz, 1H), 7.26 (t, J = 3.9 Hz, 1H), 7.03 (q, J = 8.3 Hz, 8H), 6.90 (d, J = 7.9 Hz, 4H), 6.63 – 6.55 (m, 4H), 2.29 (s, 6H), 2.21 (s, 6H). HRMS (ESI-MS) m/z : $[\text{M} - 2\text{MeCN}]^{2+}$ ($\text{C}_{42}\text{H}_{42}\text{N}_8\text{Rh}_2$) 432.0812 calc. $[\text{M} - 3\text{MeCN}]^{2+}$ ($\text{C}_{42}\text{H}_{42}\text{N}_8\text{Rh}_2$) 432.0816.

$\text{cis-}[\text{Rh}_2(\mu\text{-DTolF})_2(\mu\text{-qxnp})(\text{CH}_3\text{CN})_3][\text{BF}_4]_2$ (**2**). Quantities of $\text{cis-}[\text{Rh}_2(\mu\text{-DTolF})_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ (50.7 mg, 0.047 mmol) and qxnp (12.2 mg, 0.047 mmol) were added to a Schlenk flask with 20 mL of dry acetonitrile and refluxed in an oil bath at 110 °C for 30 minutes. The resulting dark orange solution was evaporated under vacuum to near dryness and diethyl ether was added to precipitate the product which was filtered under vacuum through a fine frit and washed with diethyl ether to yield 43.5 mg of a dark brown powder (76 %). Orange needle-like crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a concentrated solution of the compound in acetonitrile. ^1H NMR (500 MHz, CD_3CN) δ 9.75 – 9.71 (m, 2H), 8.95 – 8.88 (m, 1H), 8.83 (dd, J = 8.4, 2.0 Hz, 2H), 8.68 (d, J = 8.8 Hz, 1H), 8.06 (d, J = 8.1 Hz, 1H), 8.00 (dd, J = 8.2, 5.2 Hz, 1H), 7.87 – 7.82 (m, 2H), 7.53 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.22 – 7.19 (m, 3H), 7.12 – 7.02 (m, 4H), 7.00 (d, J = 8.4 Hz, 1H), 6.98 – 6.94 (m, 2H), 6.87 (d, J = 8.0 Hz, 2H), 6.31 – 6.27 (m, 2H), 2.48 (s, 3H), 2.28 (s, 3H), 2.19 (s, 3H), 1.83 (s, 3H). HRMS (ESI-MS) m/z : $[\text{M} - 3\text{MeCN}]^{2+}$ ($\text{C}_{46}\text{H}_{40}\text{N}_8\text{Rh}_2$) 910.1454 calc. $[\text{M} - 3\text{MeCN}]^{2+}$ ($\text{C}_{46}\text{H}_{40}\text{N}_8\text{Rh}_2$) 910.1486.

$\text{trans-}[\text{Rh}_2(\mu\text{-DTolF})_2(\mu\text{-qxnp})(\text{CH}_3\text{CN})_3][\text{BF}_4]_2$ (**3**). The partially solvated precursor $\text{cis-}[\text{Rh}_2(\text{DTolF})_2(\text{MeCN})_6][\text{BF}_4]_2$ (99.9 mg, 0.093 mmol) and an equimolar amount of qxnp (24.1 mg, 0.093 mmol) were suspended in 20 mL of acetonitrile. The mixture was refluxed for 24 h in an oil bath at 110 °C which led to the formation of a dark orange solution over the period of ~ 2 h. The reaction was cooled to room temperature and the solvent was evaporated to near dryness. Diethyl ether was added to precipitate the product which was collected by filtration under vacuum through a fine frit and washed with diethyl ether. The resulting dark orange-green powder was purified by flash column chromatography packed with silica gel using 5% MeOH in dichloromethane as the eluent to yield 27.2 mg of a dark orange powder (24 %). X-ray quality crystals were obtained by layering a concentrated solution of the product in acetonitrile with toluene. ^1H NMR (500 MHz, CD_3CN) δ 9.65 (s, 1H), 9.40 (d, J = 5.3 Hz, 1H), 9.01 (d, J = 8.7 Hz, 1H), 8.91 (dd, J = 8.2, 1.6 Hz, 1H), 8.86 (d, J = 8.8 Hz, 1H), 8.21 (d, J = 8.2 Hz, 1H), 8.00 – 7.91 (m, 3H), 7.87 (ddd, J = 8.4, 6.4, 2.0 Hz, 1H), 7.22 (t, J = 2.8 Hz, 2H), 7.01 (d, J = 8.2 Hz, 4H), 6.59 (d, J = 8.2 Hz, 4H), 6.26 (d, J = 8.1 Hz, 4H), 6.08 (d, J = 8.2 Hz, 4H), 2.25 (s, 3H), 2.15 (s, 6H), 1.82 (s, 3H). HRMS (ESI-MS) m/z : $[\text{M} - 3\text{MeCN}]^{2+}$ ($\text{C}_{46}\text{H}_{40}\text{N}_8\text{Rh}_2$) 910.1440 calc. $[\text{M} - 3\text{MeCN}]^{2+}$ ($\text{C}_{46}\text{H}_{40}\text{N}_8\text{Rh}_2$) 910.1486.

$\text{trans-}[\text{Rh}_2(\mu\text{-DTolF})_2(\mu\text{-qxnp})_2][\text{BF}_4]_2$ (**4**). Equimolar quantities of **3** (98.9 mg, 0.082 mmol) and qxnp (21.2 mg, 0.082 mmol) were suspended in 20 mL of chlorobenzene/acetonitrile (1:1) and refluxed in an oil bath for 24 h at 130 °C. The cooled reaction solution was

concentrated by evaporation under reduced pressure and diethyl ether was added. The resulting brown product was filtered through a fine frit under vacuum and washed with copious amounts of diethyl ether. To separate the final product from **5**, a short silica gel column using CH₂Cl₂/MeOH 90:10 as the eluent was used. The solvent was evaporated under reduced pressure and diethyl ether was added to precipitate the product. The resulting orange-brown powder was recrystallized by slow diffusion of diethyl ether into a solution of acetonitrile to yield 28.5 mg (26 %) of dark orange X-ray quality crystals. ¹H NMR (500 MHz, CD₃CN) δ 10.32 (d, *J* = 5.6 Hz, 2H), 9.64 (s, 2H), 9.10 (d, *J* = 8.0 Hz, 2H), 9.04 (d, *J* = 8.8 Hz, 2H), 8.80 (d, *J* = 8.7 Hz, 2H), 8.32 (dd, *J* = 8.0, 4.7 Hz, 2H), 8.10 (d, *J* = 9.0 Hz, 2H), 7.98 (t, *J* = 8.2 Hz, 2H), 7.86 (t, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 9.0 Hz, 2H), 7.10 (t, *J* = 2.6 Hz, 2H), 6.30 (d, *J* = 7.9 Hz, 8H), 5.72 (d, *J* = 8.2 Hz, 8H), 1.89 (s, 12H). HRMS (ESI-MS) *m/z*: [M + BF₄]⁺ (C₆₂H₅₀N₁₂BF₄Rh₂) 1255.240102 and [M]²⁺ (C₆₂H₅₀N₁₂Rh₂) 584.118165 calc. [M + BF₄]⁺ (C₆₂H₅₀N₁₂BF₄Rh₂) 1255.242061 and [M]²⁺ (C₆₂H₅₀N₁₂Rh₂) 584.119572.

Instrumentation and methods. ¹H NMR spectra were obtained on an Inova 500 MHz spectrometer; the chemical shifts were referenced to the residual peak of the residual CD₃CN-*d*₃ deuterated solvent signal at 1.96 ppm.⁴⁹ The activation energy of the isomerization reaction from the *cis* to the *trans* isomer was determined by preparing *cis*-[Rh₂(μ-DTolF)₂(μ-qxnp)(CH₃CN)₃][BF₄]₂ solutions in CD₃CN-*d*₃ which were placed in an oil bath at temperatures ranging from 64 – 80 °C (with 4 °C increments) and monitored by ¹H NMR spectroscopy. The resonance at 9.74 ppm corresponds to two H atoms of the *cis* isomer and was set to an integration of 2. The peak at 9.64 ppm for the *trans* isomer, corresponding to one H atom of the complex was integrated and referenced to the former feature (Figure S1). The relative integrations with respect to the total integration for the *cis* and *trans* isomers were used to calculate a percentage of converted *cis* isomer. The conversion was plotted over time, and the rate of the reaction was obtained from a mono-exponential decay fitting for each temperature. The activation energy for the isomerization was determined through an Arrhenius plot of ln(*k*) vs 1/*T*. The qxnp addition reaction was monitored over time by ¹H NMR methods. Electronic spectroscopy was performed on a Hewlett-Packard 8453 diode array spectrometer or on a Shimadzu UV-1601PC spectrophotometer in 1 × 1 cm quartz cuvettes. Extinction coefficients were determined in triplicate.

Single crystals of **1** – **4** were selected from [®]Paratone oil under ambient conditions using a MiTeGen microloop. The crystals were placed in a cold N₂ stream (**1**, **3**, and **4** at 110 K and **2** at 140 K) on a Bruker D8-QUEST diffractometer equipped with an IμS Mo microsource (λ = 0.71073 Å). Initial unit cells determined using SAINT from a set of three ω-scans consisting of 0.5° frames and a sweep width of 15° were used for the data collection strategies to collect all independent reflections to a resolution of at least 0.83 Å. Full details of the data collection and refinement parameters are presented in Table S1. The data were

corrected for absorption using SADABS,⁵⁰ and the space group was determined from analysis of the systematic absences using XPREP. The structures were solved using the intrinsic phasing routine in SHELXT or by direct methods implemented in SHELXS. The non-hydrogen atoms were located from Fourier difference maps by least-squares refinement of the structure using SHELXL-2014.⁵¹ All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions and refined with thermal parameters constrained to their parent atom. Specific details of the refinements are presented in Table S1.

Electrochemical measurements for **4** (1 × 10⁻³ M) were recorded under nitrogen in dry acetonitrile with 0.1 M [n-Bu₄N][PF₆] as the supporting electrolyte using a CH Instruments electrochemical analyzer model CH1620A. A three-electrode cell was used with a glassy carbon disc working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode standardized to ferrocene (*E*_{1/2} = +0.55 V vs Ag/AgCl). Electrospray ionization mass spectrometry (ESI-MS) data were obtained in the Laboratory for Biological Mass Spectrometry at Texas A&M University using a Thermo Scientific Q Exactive Focus. The sample was directly infused at a flow rate of 10 μL/min. The Q Exactive Focus HESI source was operated in full MS in positive mode. The mass resolution was tuned to 17500 FWHM at *m/z* 200, the spray voltage was set to 3.75 kV, and the sheath gas and auxiliary gas flow rates were set to 7 and 0 arbitrary units, respectively. The transfer capillary temperature was held at 250 °C and the S-Lens RF level was set at 50 v. Exactive Series 2.8 SP1/Xcalibur 4.0 software was used for data acquisition and processing.

Ultrafast transient absorption experiments were performed on a previously described system.⁵² Briefly, the output of a Ti:sapphire regenerative amplifier (Astrella 1K-USP, Coherent) was split to generate the white light probe through a rotating CaF₂ crystal and to a pump an OPA (OPerA Solo, Coherent/Positive Light) to generate the pump pulse at 600 nm. A thermally cooled CCD camera with home-built software written in LabVIEW 2015 was used to collect and manipulate the data. The sample solution was prepared with ~ 0.5 OD at the excitation wavelength and ~ 5 mL solution containing the sample was flowed through a 1 mm path-length Harrick Scientific flow cell (1 mm thick CaF₂ windows) and excited with ~ 2.5 μJ at the pump wavelength. An instrument response of fwhm ~ 85 fs was measured using the Kerr effect in cyclohexane. The polarization angle between the pump and probe was set to 54.7° to avoid rotational diffusion effects. Nanosecond transient absorption spectroscopy was performed on a previously reported instrument.⁵³ For these experiments, the 600 nm excitation pulse was generated from an OPO (basiScan, Spectra-Physics) pumped by the third harmonic (355 nm) of a Nd:YAG laser (Quanta-Ray INDI, Spectra-Physics) and the output of a continuous 150 W xenon arc lamp gated using a Uniblitz shutter was used as the probe. The excitation and probe pulses were overlapped at a 90° geometry at the sample. The spectral

measurements were collected on a spectrometer (LP 980, Edinburgh Instruments) equipped with an ICCD camera. Sample concentrations were adjusted such that they absorbed ~ 0.5 at the excitation wavelength in a 1×1 quartz cuvette.

Density Functional Theory (DFT) calculations were performed to calculate the molecular and electronic structures of complexes **1** – **4** using the Gaussian (09) program package.⁵⁴ The Stuttgart RSC 1997 Electron Core Potential (ECP)⁵⁵ basis set was used for the Rh atoms, the 6-31G+ basis set for the C, N, and H atoms,⁵⁶ and B3LYP^{57, 58} correlation and exchange functionals were used. For the calculation of the energies of the intermediates, Grimme's dispersion correction (D3)⁵⁹ was included in the optimization using a polarized continuum model (PCM)⁶⁰ with acetonitrile. As a starting point for the gas-phase optimizations, geometric parameters were taken from the crystal structures for the complexes; interstitial solvent molecules and counterions were omitted. For the theoretical molecule, *trans*-[Rh₂(DTolF)₂(np)(MeCN)₄][BF₄]₂, the geometrical parameters of complex **1** were used as a starting point and modified in 'Agui' to build the corresponding *trans* isomer. A similar procedure was employed for building the postulated intermediates *cis/trans*-[Rh₂(μ-DTolF)(κ-DTolF)(qxnP)(MeCN)₃]²⁺ and *cis/trans*-[Rh₂(μ-DTolF)(κ-DTolF)(np)(MeCN)₄]²⁺. Following gas-phase optimization, Time-Dependent Density Functional Theory (TD-DFT)⁶¹ calculations were performed using PCM with acetonitrile as the solvent. The first sixty lowest singlet-to-singlet excited states were calculated from the optimized singlet ground state. Single point energy calculations at different bond lengths ranging from 2 to 50 Å were used to estimate the Rh-N bond dissociation energies for the equatorial and axial acetonitrile molecules of *cis/trans*-[Rh₂(μ-DTolF)₂(qxnP)(MeCN)₃]²⁺ (Figure S2). A relaxed potential energy scan calculation with 10 steps of 0.5 Å was carried out to estimate the Rh-N_{DTolF} bond dissociation energy for the *cis*-[Rh₂(μ-DTolF)₂(qxnP)(MeCN)₃]²⁺ complex. The graphic software 'Agui'⁶² with an isovalue = 0.04 was used to plot molecular orbitals (Table S2). In order to estimate the bond dissociation energies for the axial and equatorial acetonitrile molecules in **2** and **3**, single point energy calculations at different Rh-NCCH₃ distances were performed using the gas-phase optimized structures as a starting point. The Chemissian program⁶³ was used to perform Natural Transition Orbital (NTO) analyses.

RESULTS AND DISCUSSION

Synthesis. Compounds **1** – **4** were synthesized by a methodology that was optimized to control the geometric isomerism of the products (Scheme 1). The syntheses and isolation of the mono-substituted complexes **1** – **3** are influenced by stoichiometry, temperature, and reaction time.

Compound **1** was synthesized in refluxing acetonitrile from a 1:1 ratio of the np ligand and *cis*-

[Rh₂(DTolF)₂(CH₃CN)₆][BF₄]₂ as depicted in Scheme 1. Complexes **2** and **3** were also prepared in acetonitrile from a 1:1 ratio of the qxnP ligand and the same dirhodium partial-paddlewheel starting material as depicted in Scheme 1 but under different conditions. In the case of **2**, the 1:1 mixture was refluxed in acetonitrile for 30 minutes, or was heated for 24 h at 40 °C. Both reactions yielded **2** along with a small amount of **5** (12% as determined by ¹H NMR spectroscopy of the crude product which were separated by slow diffusion of diethyl ether into a concentrated solution of the mixture in acetonitrile to yield pure crystals of **2**. The thermodynamic product, compound **3**, was obtained by refluxing the initial equimolar mixture of starting materials for 24 h, as the isomerization from the *cis* isomer **2** to the *trans* analog **3** is a slow kinetic process that requires the migration of a DTolF ligand. The direct conversion of *cis*-[Rh₂(μ-DTolF)₂(MeCN)₆][BF₄]₂ to **3** upon addition of one equivalent of ligand does not occur as evidenced by ¹H NMR spectra obtained before and after refluxing the dirhodium starting material in acetonitrile (Figure S3). A 24 h reflux of the *cis*-[Rh₂(μ-DTolF)₂(MeCN)₆][BF₄]₂ compound alone does not yield *trans*-[Rh₂(μ-DTolF)₂(MeCN)₆][BF₄]₂ and, furthermore, does not alter the ratios of **2** and **3** obtained after addition of the ligand (Figure S4). The product was purified by layering a concentrated solution of the compound in acetonitrile with toluene. As demonstrated by ¹H NMR spectral experiments, compound **3** is also obtained in quantitative yields by refluxing **2** for 48 h in acetonitrile and heating to temperatures near the boiling point of the solvent (Figure S5).

The synthesis of **4** is substantially different from those used to isolate the other complexes, as no reaction occurs when qxnP is refluxed in the presence of **3** in acetonitrile. In order to obtain the *trans* bis-substituted complex **4**, it was necessary to reflux **3** in a non-coordinating solvent with a high boiling point. A 24-hour reflux of a 1:1 mixture of qxnP and the *trans* intermediate **3** in a 1:1 chlorobenzene /acetonitrile mixture yielded **4** as the final product (Scheme 1).

X-ray Crystal Structures. The molecular structures of complexes **1** – **4** (Figures 2 and 3) were determined by single crystal X-ray diffraction experiments. The dicationic compounds consist of a dirhodium core bridged by two anionic N,N'-(p-tolyl)formamidinate ligands with two [BF₄]⁻ anions. Compound **1** is a 1,8-naphthyridine monosubstituted complex with two equatorial and two axial acetonitrile molecules. Complexes **2** and **3** contain a quinoxaline derivatized naphthyridine ligand (qxnP) that binds to one of the axial positions, leaving only one acetonitrile molecule to occupy the second axial site, whereas **4**, with two qxnP ligands, is fully axially-blocked. The Rh-Rh bond distances are 2.5049(7) Å, 2.49896(11) Å, 2.50067(14) Å, and 2.4942(8) Å for compounds **1** – **4**, respectively, longer than the Rh-Rh bond distance of 2.4498(2) Å for compound **5** (Table S3).²⁴

Scheme 1. Syntheses of complexes 1 – 5: a) 1 equivalent of 1,8-naphthyridine in refluxing acetonitrile for 24 h, b) qxnp (2-(1,8-naphthyridin-2-yl)quinoxaline) in refluxing acetonitrile for 30 minutes or stirring in acetonitrile at 40 °C for 24 h, c) 1 equivalent of qxnp in refluxing acetonitrile for 24 h, d) refluxing acetonitrile for 24 h, e) 1 equivalent of qxnp in refluxing acetonitrile for 24 h, and f) 1 equivalent of qxnp in a mixture of refluxing 1:1 chlorobenzene/acetonitrile for 24 h.

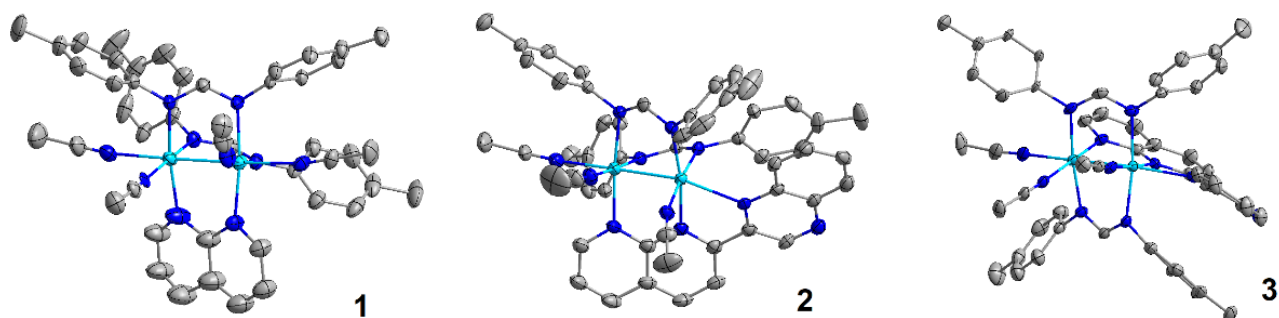
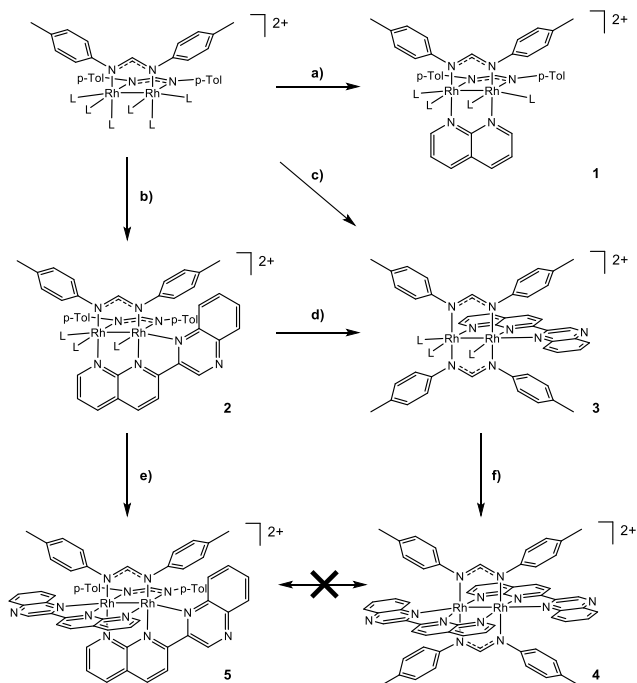


Figure 2. Thermal ellipsoid plots for **1** – **3**, drawn at the 50% probability level. Counterions, interstitial solvent molecules, and hydrogen atoms were omitted for the sake of clarity.

Compounds **1** – **3** and **5** exhibit N_{eq} -Rh-Rh- N_{eq} torsion angles that range between 17–23°, attributed to the steric strain from the equatorial acetonitrile molecules in **1** – **3** and π - π stacking interactions as well as steric strain between the DTolF ligands in **5**. In contrast, the torsion angle of **4** is only -1.3337(4)°, which results in a near-perfect alignment with the N-C-N moiety of the bridging formamidinate ligand (Figure 3b). The longer Rh-Rh bond distances for **1** – **3** as compared to that of **5** is not surprising given that **5** has four bridging ligands as opposed to three bridges in **1** – **3**. In addition, all of the Rh-Rh bond distances are consistently shorter than those for complexes with κ -chelating ligands, e.g., 2.5818(3) Å for *cis*-[Rh₂(DTolF)₂(dppn)₂][BF₄]₂,³² due to the presence of a third (**1** – **3**) or fourth (**4** and **5**) bridging np or qxnp moiety. The bite angle of the π -accepting qxnp ligand results in

considerable deviation from linearity of the Rh-Rh- N_{ax} bond angles in **2** – **5**, 159.6559(12)°, 162.5328(14)°, 165.539(4)°, and 161.73(4)°, respectively which results in longer Rh- N_{ax} (qxnp) bond distances for **2** and **3** of 2.16872(9) Å and 2.14851(12) Å, respectively and concomitant shortening of the Rh-NCCH₃ axial bond on the other rhodium metal center.

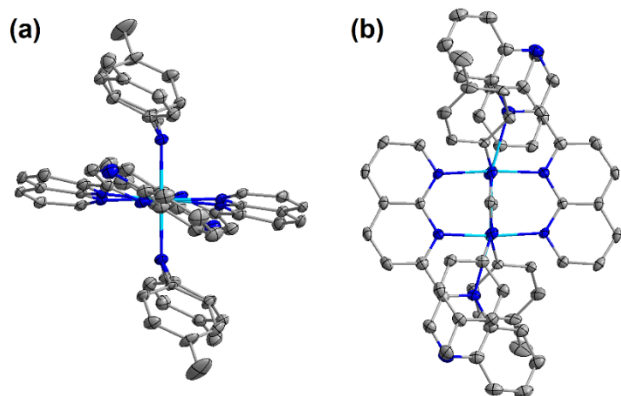


Figure 3. Thermal ellipsoid plots for **4**, drawn at the 50% probability level: view looking down the rhodium-rhodium bond axis (a) and top view (b). Counterions, interstitial solvent molecules, and hydrogen atoms were omitted for the sake of clarity.

Compounds **2** – **5** engage in intramolecular π - π stacking interactions between the *p*-tolyl substituents of the formamidinate bridging ligands and the quinoxalinyll moieties of the axially blocking qxnp ligands (Figure S6). Given that the *cis* and *trans* complexes have distinct molecular geometries, the distances between the rings range from 3.348 Å to 3.654 Å in the series. Changes in symmetry and intramolecular interactions are consistent with the chemical shifts observed in the ^1H NMR spectra of these complexes, particularly in the quinoxalinyll moiety. These shifts provide a useful spectroscopic tool for differentiating between the complexes and to study the kinetics of the incorporation of qxnp ligands and the isomerization reactions.

Electrochemistry and Electronic Absorption Spectroscopy. The electrochemical data for **4** are presented in Table 1 and Figure S7 along with the previously reported

data for **5**. Compound **4** displays a one-electron reversible couple at $E_{1/2} = +1.00$ V vs Ag/AgCl in acetonitrile (0.1 M Bu_4NPF_6) which is an oxidation of the metal-formamidinate HOMO, as assigned for **5** and related formamidinate-bridged dirhodium(II,II) complexes,^{25, 64} and a one-electron reduction of one of the qxnp π -accepting ligands at $E_{1/2} = -0.34$ V vs Ag/AgCl. This reduction potential is more positive than that observed for **5** and other axially blocked complexes such as *cis*- $[\text{Rh}_2(\text{DTolF})_2(\text{L})_2][\text{BF}_4]_2$, where L = 2-(pyridin-2-yl)-1,8-naphthyridine or 2-(quinolin-2-yl)-1,8-naphthyridine) of $E_{1/2} = -0.70$ V vs Ag/AgCl and $E_{1/2} = -0.62$ V vs Ag/AgCl respectively, indicating that **4** is easier to reduce, a point that will be discussed in the DFT calculations section.

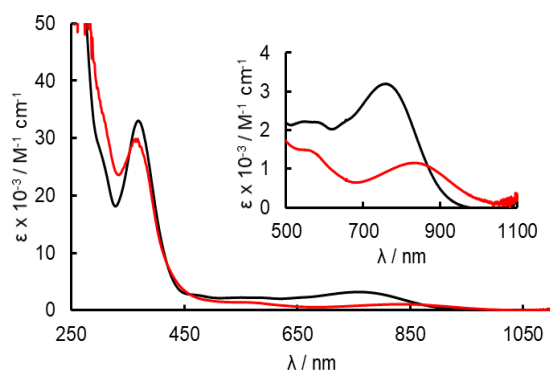


Figure 4. Electronic absorption spectra of **4** (red) and **5** (black).

A comparison of the steady state absorption spectra of **4** and **5** is presented in Figure 4, and the maxima, λ_{abs} , with their corresponding molar extinction coefficients, ϵ , are listed in Table 1. Compound **4** exhibits intense absorption maxima in the ultraviolet region at 258 nm and 367 nm, similar to those reported for **5** at 259 nm and 369 nm (Table 1). These absorption peaks of

Table 1. Electronic Absorption Maxima (λ_{abs}), Molar Absorptivities (ϵ), Reduction Potentials ($E_{1/2}$), Singlet (τ_{S}) and Triplet (τ_{T}) Lifetimes for **4 and **5** in Acetonitrile.**

Complex	λ_{abs} / nm (ϵ / $\times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	$E_{1/2}$ / V ^b	τ_{S} / ps ^c	τ_{T} / ns ^c
4	258 (124), 367 (47), 560 (2.3), 832(1.9)	+1.00, -0.34	3	0.40
5 ^a	259 (83), 369 (32), 554 (2.2), 758(3.2)	+1.08, -0.43	8	7.2

^aFrom reference 24. ^bvs Ag/AgCl in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$. ^cFrom transient absorption experiments at 298 K ($\lambda_{\text{exc}} = 600$ nm, fwhm = 85 fs).

4 and **5** are similar to those observed for the free qxnp ligand in CH_2Cl_2 , 254 nm ($\epsilon = 99(13) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) and 342 nm ($\epsilon = 70(8) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), and are assigned as ligand-centered $^1\pi\pi^*$ transitions. There is minimal shift in the peak at 560 nm in **4** to 554 nm in **5**. In contrast, the lowest energy transition of **4** at 832 nm ($12,020 \text{ cm}^{-1}$) is shifted bathochromically from the 758 nm ($13,190 \text{ cm}^{-1}$) maximum recorded for **5** and is assigned as $^1\text{ML-LCT}$ with $\text{Rh}_2/\text{DTolF} \rightarrow \text{qxnp}(\pi^*)$ character. The 74 nm ($1,170 \text{ cm}^{-1}$) red shift of this transition is consistent with the more easily reduced qxnp ligand by 0.09 V in **4** as compared

to that in **5**, together with a more easily oxidized Rh_2/DTolF HOMO in **4** relative to **5** (Table 1).

Electronic Structure Calculations. DFT calculations were performed to assess the contributions of atomic orbitals to the molecular orbitals (MOs) in these dirhodium cations and to better understand the chemistry that leads to formation of the *trans*-substituted dirhodium complexes. The geometrical parameters of the crystal structures of complexes **1** – **4** were used as starting points. The energies of the metal-metal bonding MOs are $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^4(\delta^*)^2(\sigma^*)^0$ in **1** – **5** due to the presence of strong π -donor formamidinate ligands with the

correct symmetry to interact with the $\text{Rh}_2(\delta^*)$ MO. This interaction raises the energy of the $\text{Rh}_2(\delta^*)$ MO such that it lies above the $\text{Rh}_2(\pi^*)$ orbital. This electronic configuration is a departure from archetypal d^7 - d^7 dinuclear complexes with weaker π -donor bridging ligands for which the molecular orbital levels are $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2(\pi^*)^4(\sigma^*)^0$, but is consistent with other formamidinate containing complexes.^{65, 66}

The calculations reveal that the HOMOs in **1** – **4** possess 25–34% $\text{Rh}_2(\delta^*)$ and 63–72% formamidinate contributions (Table S4). These results are in accord with related dirhodium formamidinate complexes including the previously reported compound **5** which has a 31% contribution from the $\text{Rh}_2(\delta^*)$ MO and 63% from the formamidinate ligand.^{24, 25} The LUMOs of **1** – **4** are primarily localized on the π -accepting ligand, np or qxnp, as expected from prior work.^{24, 25} Compound **1** has an orbital contribution to the LUMO of only 66% from the np ligand, whereas the LUMOs of **2** – **4** possess qxnp contributions that range from 89% to 94%.

The *trans* bis-substituted compound **4** displays a nearly perfectly eclipsed configuration when viewed down the Rh-Rh bond (Figure 3a) while the other complexes exhibit more distorted structures due to the steric strain caused by the *p*-tolyl moieties of the formamidinate bridging ligands as well as the presence of intramolecular π -stacking interactions between the quinoxalinylligands and the *p*-tolyl groups (Figure S6). The eclipsed conformation of **4** increases the electron donation from the electron-rich bridging ligands to the $\text{Rh}_2(\delta^*)$ MO which raises the energy of the HOMO leading to a weaker σ -bond. As a consequence, this results in a longer Rh-Rh bond of 2.4942(8) Å compared to **5**, Rh-Rh = 2.4498(2) Å (Figure 5).²⁴ In addition, the elongation of the Rh-Rh bond and concomitant shortening of the Rh- N_{ax} distance is a reflection of an increase in the axial σ -donation of the quinoxalinylligand which raises the energy of the $\text{Rh}_2(\sigma^*)$ molecular orbital. The LUMO of **4** is primarily qxnp in character and is calculated to lie at -0.0898 eV lower in energy than the qxnp-based LUMO of **5**. This difference is attributed to the variation in orbital overlap between **4** and **5**; the $\text{Rh}_2(\delta^*)$ is interacting with two formamidinate bridging ligands in **4**, whereas, in **5**, two lobes of this orbital are shared by the formamidinate ligands (Table S2). This difference in participation of the dirhodium core in bonding to the formamidinate ligands translates to increased electron density on the qxnp ligands positioned *trans* to DTolF in the *cis* isomer **5**, rendering the compound more difficult to reduce.

The lowest energy transition observed in the steady state absorption spectrum of **4** appears in the near-IR region, extending beyond 950 nm with a maximum at 832 nm, which is red-shifted by $1,170\text{ cm}^{-1}$ as compared to **5**. The TD-DFT calculations predict this transition at 938 nm and 878 nm for **4** and **5**, respectively, and reveal that it is primarily HOMO-LUMO in nature and ¹ML-LCT in character. The difference in energies between the calculated and experimentally determined ¹MLCT bands are consistently red-shifted in both compounds which can be attributed to the limitations of DFT calculations.⁶⁷ The second lowest energy transition is predicted to occur at 661 nm for **4** and 684 nm for **5** and is HOMO-1 → LUMO in character (Table S5).

In order to elucidate the mechanism of DTolF migration, optimization calculations with Grimme's dispersion corrections and a polarized continuum model with acetonitrile were undertaken for **2** and **3** and for two possible

intermediates (Figures S8 and S9).⁶⁸⁻⁷⁰ The calculated species, *cis/trans*- $[\text{Rh}_2(\mu\text{-DTolF})(\kappa\text{-DTolF})(\text{qxnp})(\text{MeCN})_3]^{2+}$ and *cis/trans*- $[\text{Rh}_2(\mu\text{-DTolF})(\kappa\text{-DTolF})(\text{np})(\text{MeCN})_3]^{2+}$, are proposed as intermediates in a pathway for migration of the formamidinate bridging ligand. The logical first step of the migration is $\text{Rh}_1\text{-N}_1$ bond scission, rotation along the remaining $\text{Rh}_2\text{-N}_2$ bond, and binding of the N_1 to Rh_2 in the axial position by displacement of the axial MeCN molecule. The second step is postulated to involve binding of N_2 to the Rh_2 , but in a *trans* configuration, to produce the mono-substituted *trans* isomer **3** (Figure 6). The calculated energies for these intermediates, the *cis/trans*- $[\text{Rh}_2(\mu\text{-DTolF})_2(\text{qxnp})(\text{MeCN})_3]^{2+}$ complexes, complex **1** and its theoretical *trans*- $[\text{Rh}_2(\text{DTolF})_2(\text{np})(\text{MeCN})_2]^{2+}$ analog indicate that axial chelation of the qxnp ligand has a profound effect on the energies of these axially-bound intermediates due to the *trans* influence across the $\text{Rh}_2(\sigma)$ bond from the quinoxalinylligand. The energies of the intermediates are, on average, ~ 8 kcal/mol lower in energy for the qxnp-bearing complex. These calculations are in agreement with the fact that **1** does not undergo an isomerization step to form the *trans* isomer even after 24 hours of refluxing in acetonitrile which further supports the fact that an axially chelated intermediate is present and stabilized by axial chelation. These calculations are consistent with experimentally observed phenomena reported in axially blocked Mo-Mo complexes in which axial chelation allowed for the synthesis of the *trans* isomers.^{71, 72} In addition, the synthesis of the axially chelated compound *cis*- $[\text{Rh}_2(\text{OAc})_2(\text{pynp})_2]$ (pynp = 2-(pyridin-2-yl)-1,8-naphthyridine) was carried out in refluxing acetonitrile whereas the synthesis of *trans*- $[\text{Rh}_2(\text{OAc})_2(\text{L})_2]$ and *trans*- $[\text{Rh}_2(\text{OAc})_2(\text{L}')_2]$ (L = 2-(pyrazin-2-yl)-1,8-naphthyridine and L' = 2-(1,8-naphthyridin-2-yl)thiazole) were carried out at room temperature. These results underscore the fact that *cis*- Rh_2 isomers are obtained under kinetic conditions and that the formation of the *trans* analogs is facilitated under thermodynamic conditions.^{73, 74}

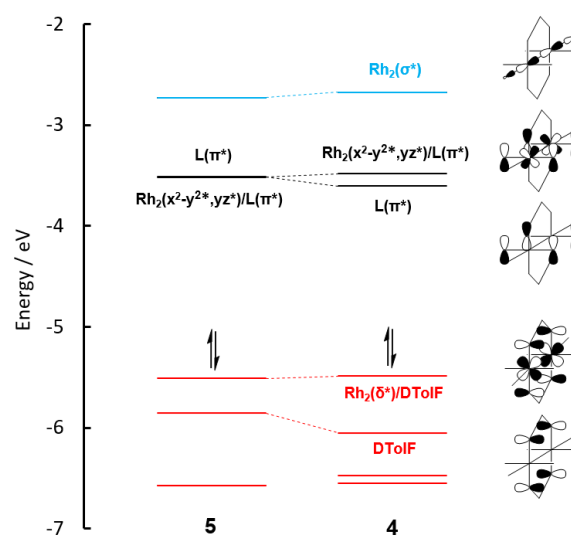


Figure 5. Calculated MO diagrams for the *cis* (**5**) and *trans* (**4**) compounds.

The energies of complexes **4** and **5** were also calculated and compared with those of **2** and **3** as a function of a stepwise

qxnp addition reaction (Figure S10). The computations indicate that there is no significant energy difference between the *cis* and *trans* bis-substituted compounds **4** and **5**, which indicates that both isomers should be synthetically accessible. There is, however, a large difference in energy between **2** and **3** which allows for the isolation of these compounds and the formation of **5** and **4** respectively, upon addition of a second equivalent of qxnp ligand. The calculated energies are in agreement with experimental observations regarding the isolation of **2** and **3**, for which a significant amount of complex **5** is obtained due to the energetically favored nature of the reaction.

The synthesis of the final *trans* complex **4** does not occur by treating **3** with one equivalent of qxnp ligand in refluxing acetonitrile. In order to gain understanding into the synthetic requirements for this reaction, energy calculations were performed for **2** and **3** as functions of the Rh-MeCN_{ax} and Rh-MeCN_{eq} bonds (Table S6), the results of which indicate a significant difference in the equatorial acetonitrile binding energies for the two isomers. Compound **3** has weaker calculated axial interaction energies and stronger equatorial Rh-N interactions for the acetonitrile ligands than those of complex **2**. This behavior is consistent with the geometric arrangement of the formamidinate bridging ligands. In **2**, the formamidinate ligand, known to exert a strong *trans* effect, facilitates Rh-MeCN_{eq} ligand exchange with the π -accepting ligands.⁴⁴ Compound **3** has a marginally stronger Rh-MeCN_{eq} bond based the bond distances and the results of DFT calculations and requires higher energies to promote ligand exchange, consistent with experimental observations. In this case it was necessary to use a non-coordinating solvent with a higher boiling point to obtain the desired bis-substituted *trans* complex **4**.

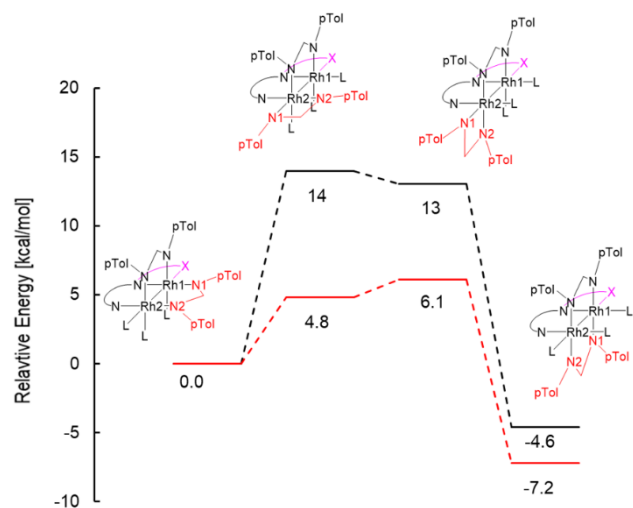


Figure 6. Energies of the *cis*-[Rh₂(DTolF)₂(np)(MeCN)₄][BF₄]₂ and *cis*-[Rh₂(DTolF)₂(qxnp)(MeCN)₃][BF₄]₂ starting materials relative to the corresponding *trans* products, along with those of the proposed intermediates of DTolF migration. The red line corresponds to the *cis-trans* isomerism reaction of the axially blocked complexes (X = quinoxaliny axially-blocking moiety) and the black line corresponds to the isomerism reaction of the axially free (X = MeCN) complexes.

Kinetic Studies. In order to determine the activation energy of the isomerization reaction from **2** to **3**, solutions of *cis*-[Rh₂(μ -DTolF)₂(μ -qxnp)(CH₃CN)₃][BF₄]₂ in CD₃CN-d₃ were placed in an oil bath at temperatures ranging from 64 – 80 °C (with 4 °C increments) and monitored by ¹H NMR spectroscopy. Owing to differences in the symmetry of the complexes and the resulting changes in the intramolecular π - π stacking interactions (Figure S6), the quinoxaliny moiety of the axial blocking ligand displays markedly different chemical shifts for **2** and **3** that allow for the reaction to be followed by ¹H NMR spectroscopy (Figure 7). For **2**, the area of the peak that corresponds to two hydrogen atoms of the quinoxaliny moiety at 9.74 ppm was set to a value of 2. The transformation of **2** to **3** was then referenced to the total area of the latter species, which exhibits a resonance at 9.64 ppm for the hydrogen atom in the quinoxaliny moiety. The percent transformation of **2** was calculated and plotted over time and the rate of reaction for each temperature was obtained from a mono-exponential decay fitting (Figure 7b), which is consistent with the appearance of **3**. The conversion takes place over 24 h in refluxing acetonitrile which allows for the isolation of complex **3** at relatively short reaction times. The reaction is significantly slower at 60 °C, however, and requires four days to achieve full conversion of **2** to **3**. The reaction performed at 40 °C did not yield the *trans* isomer over a 24 h period and was used to isolate **2**. An activation energy of 38 kcal/mol was determined from a linear fit of an Arrhenius plot of the logarithm of the observed rates of reaction versus reciprocal temperature (Figure S11). This activation energy is consistent with a rate-limiting step involving Rh-N_{DTolF} bond dissociation which is proposed as the first step for the DTolF migration, in agreement with the computationally calculated bond energy of 54 kcal/mol for the Rh-N_{DTolF} bond as well as previously reported Rh-N_{eq} energies of 33 kcal/mol.^{75, 76}

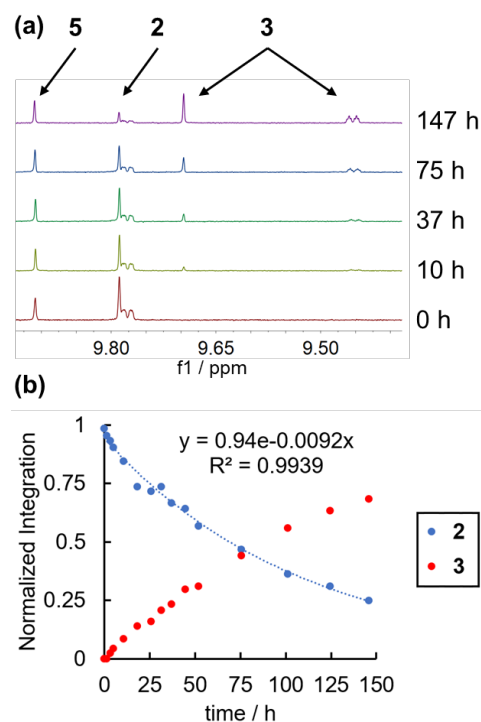


Figure 7. (a) Selected ¹H NMR spectroscopic traces following the isomerization reaction from **2** to **3** and (b)

monoexponential decay of the normalized integration for the conversion of **2** (blue) to **3** (red) at 68 °C in acetonitrile.

Time-Resolved Spectroscopy. Femtosecond transient absorption spectroscopy was performed on **4** to investigate the excited states properties of the two complexes, (Figure 8b) and compared with the results for **5** (Figure 8a). The $^1\text{ML-LCT Rh}_2(\delta^*)/\text{DTolF}(\pi^*) \rightarrow \text{qxnp}(\pi^*)$ excited state of **4** is populated upon 600 nm excitation (2.5 $\mu\text{J}/\text{pulse}$, IRF = 85 fs), leading to a broad absorption at ~ 420 nm. This state decays with a lifetime of 3 ps to the corresponding $^3\text{ML-LCT}$ excited state, and the latter regenerates the ground state with $\tau_{\text{T}} = 405$ ps in acetonitrile. The kinetic trace of the signal at 420 nm was fitted biexponentially to obtain the lifetimes of the two states (Figure S12). The singlet and triplet lifetimes for **4**, $\tau_{\text{S}} = 3$ ps and $\tau_{\text{T}} = 405$ ps, respectively, are shorter than those of **5**, $\tau_{\text{S}} = 8$ ps and $\tau_{\text{T}} = 7.2$ ns (Table 1). The Energy Gap Law predicts that the lower energy $^3\text{ML-LCT}$ state in **4** should lead to faster radiationless decay and a shorter $^3\text{ML-LCT}$ lifetime as compared to **5**, but the small energy difference between the two compounds would only be expected to result in a decrease to ~ 6 ns in **4** from 7 ns in **5**. Instead, the shorter lifetimes of the excited states of **4** are attributed to its longer Rh-Rh bond as compared to **5**, which results in a more accessible metal-centered state that facilitates fast deactivation.

To evaluate potential application of **4** and **5** as dyes for DSSCs, photoinduced charge transfer from a reversible electron donor, *p*-phenylenediamine (*p*-PD) with $E_{1/2} = + 0.28$ V vs Ag/AgCl, was examined by nanosecond transient absorption spectroscopy (Figure 9). Upon 600 nm excitation (5 mJ/pulse, IRF = 6 ns), a mixture of **4** and *p*-PD (20 mM) displays a long-lived absorption difference spectrum consistent with the formation of the *p*-PD radical cation, with an absorption maximum at 460 nm.²⁴ This charge transfer is also observed for **5** but the signal is ~ 30 -fold stronger for the *p*-PD radical cation under the same experimental conditions. The differences in the efficiencies of bimolecular charge transfer between **4** and **5** are attributed to the shorter triplet lifetime of **4**. The reductive quenching of **4**, with a ground state reduction potential of -0.34 V vs Ag/AgCl (Table 1), by *p*-PD requires that the $^3\text{ML-LCT}$ state, E_{T} , of **4** lie at least 0.62 eV above the ground state. This value for E_{T} is consistent with those measured for related $\text{Rh}_2(\text{II,II})$ complexes, ~ 1.1 eV.²⁵

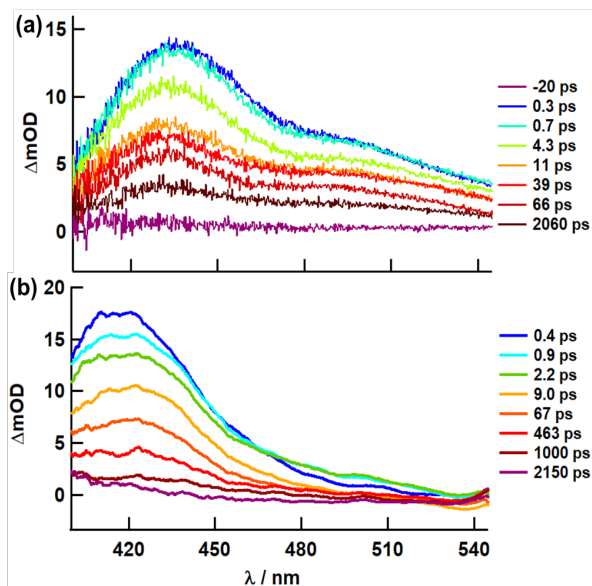


Figure 8. Transient absorption spectra of (a) the *cis* isomer **5** ($\lambda_{\text{ex}} = 720$ nm, 2.5 μJ) and (b) the *trans* isomer **4** ($\lambda_{\text{ex}} = 600$ nm, 2.5 μJ).

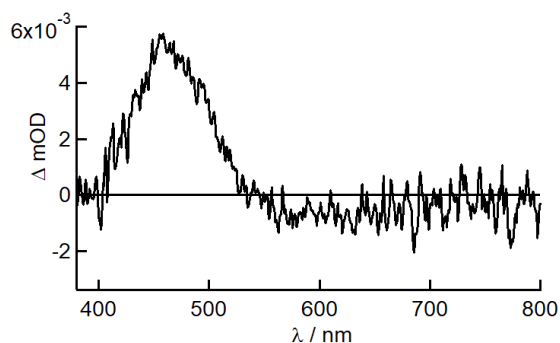


Figure 9. Transient absorption spectrum of the *trans* isomer **4** in acetonitrile (130 μM) in the presence of *p*-phenylenediamine (1:150) collected at 1 μs after the 600 nm excitation pulse (IRF = 6 ns, 5 mJ).

CONCLUSIONS

A series of four new dirhodium formamidinate complexes featuring π -accepting ligands was described in detail. A particularly important finding is the isolation of the first *trans*-formamidinate dicationic complex, **4**, by careful control of the reaction conditions used to prepare the *trans* precursor, **2**, in favor of the *cis* isomer. Compound **4** displays a panchromatic absorption profile that extends into the near-IR region with a maximum at 832 nm that corresponds to a $^1\text{ML-LCT}$ transition as predicted by TD-DFT. This absorption is red-shifted with respect to that of the corresponding *cis* complex **5**. The $^1\text{ML-LCT}$ and $^3\text{ML-LCT}$ excited state lifetimes of **4** were measured and found to be 3 ps and 0.4 ns, respectively, by transient absorption spectroscopy. Although these lifetimes are shorter than those of the *cis* analog, the $^3\text{ML-LCT}$ is sufficiently long-lived to oxidize *p*-phenylenediamine in solution, leading to an excited state energy of ≥ 0.62 eV. The smaller HOMO-LUMO gap of **4** as compared to **5** is attributed to its eclipsed configuration, which leads to better orbital overlap and a concomitant

increase in energy of the Rh-containing MOs. The synthesis of **4** was rendered possible by implementing the use of axial blocking ligands which trigger the migration of a bridging formamidinate ligand to yield the *trans* isomer in the presence of one equivalent of the qxn ligand. Calculations support the feasibility of this approach as a general route to access *trans* isomers although transition state calculations are required to provide a better understanding of the details of the formamidinate migration. It is especially noteworthy that a change in the arrangement of ligands in these molecules has little effect on photophysical and excited state redox properties, indeed the parentage of the transitions remains the same for the *cis* and *trans* isomers and the excited states of both species are reducing enough to allow them to participate in electron transfer reactions. The results of this study pave the way for a systematic investigation of the photophysical properties of hitherto unexplored *trans* isomers for potential sensitization of p-type semiconductors with low energy light in DSSCs and related solar energy conversion applications. Moreover, these new geometries can be used as new formamidinate-containing scaffolds as building blocks for supramolecular architectures with potentially interesting photophysical properties.

ASSOCIATED CONTENT

Transient absorption experiments, electron density maps, ¹H NMR kinetic experiments, electron-transfer experiments, and crystallographic information. CCDC deposition numbers: 1947645-1947648.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

K. R. D. is grateful for support from the National Science Foundation (419791-00001) and the Welch Foundation (A-1449 for summer support of A.M.). C.T. and K.R.D are thankful for partial support of this work by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (DE-SC0020243) and the National Science Foundation (CHE-1800395), as well as the ultrafast laser facility at Ohio State, the Center for Chemical and Biophysical Dynamics (CCBD). The authors acknowledge Dr. L. M. Pérez for providing software and computer time and for her assistance with the computational studies and the Super Computing Facility and the Laboratory for Molecular Simulation at Texas A&M University. The use of the TAMU/LBMS-Applications Laboratory (Laboratory of Biological Mass Spectroscopy) is also acknowledged.

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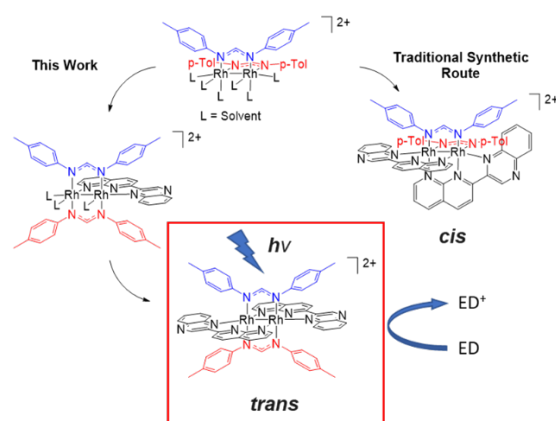
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Schematic representation of the synthetic route employed to obtain the elusive *trans* formamidinate isomer and its ability to oxidize an electron donor upon excitation with low-energy light from its excited state.
