

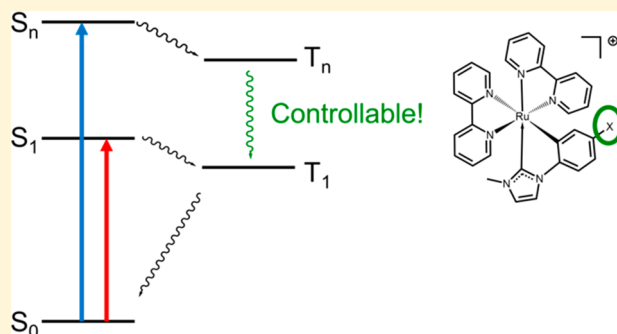
Unusually Slow Internal Conversion in N-Heterocyclic Carbene/Carbanion Cyclometalated Ru(II) Complexes: A Hammett Relationship

William T. Kender and Claudia Turro*

Department of Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio 43210, United States

 Supporting Information

ABSTRACT: A series of six $[\text{Ru}(\text{bpy})_2(\text{NHC-R})]^+$ complexes were synthesized and characterized, where $\text{bpy} = 2,2'$ -bipyridine and NHC-R is an N-heterocyclic carbene covalently linked to a carbanion with a number of substituents, $\text{R} = -\text{OMe}$ (1), $-\text{Me}$ (2), $-\text{H}$ (3), $-\text{Cl}$ (4), $-\text{CO}_2\text{Et}$ (5), and $-\text{NO}_2$ (6). The effects of these strongly σ -donating NHC-R ligands on the ground-state electronic structure and on the excited-state character and dynamics were probed using electrochemistry, TD-DFT calculations, and steady-state absorption and emission spectroscopies, along with ultrafast transient absorption and time-resolved IR measurements. The excitation of 1–5 with a 400 nm pulse ($\text{irf} = 85$ fs) results in the population of a high energy singlet state, S_n , that rapidly intersystem crosses into a high-lying triplet state, T_n . Over the course of 7–22 ps, T_n relaxes to the lowest lying triplet state, T_1 , which is metal/ligand-to-ligand charge transfer, ${}^3\text{Ru}(\text{d})/\text{NHC}(\pi) \rightarrow \text{bpy}(\pi^*)$ in character. These ${}^3\text{ML-LCT}$ states decay to regenerate the ground state with lifetimes, τ , that range from <8 to 15 ns at 298 K and from 10 to 23 ns at 77 K in CH_3CN . Both the excited-state lifetime at 77 K and the $\text{T}_n \rightarrow \text{T}_1$ rate of internal conversion of 1–5 are dependent on the substituent R, and the latter correlates with the Hammett parameter (σ^+_p) of the NHC-R ligand. Excitation of 1–5 with low energy light, 550–670 nm, does not result in the population of T_n , as only T_1 is observed. In the case of 6, excitation is expected to populate a ${}^1\text{Ru}(\text{d})/\text{NHC}(\pi) \rightarrow \text{NHC}(\pi^*)$ state localized on the NHC-NO_2 ligand, which decays to a higher energy ${}^3\text{Ru}(\text{d})/\text{NHC}(\pi) \rightarrow \text{NHC}(\pi^*)$ state followed by internal conversion to the ${}^3\text{Ru}(\text{d})/\text{NHC}(\pi) \rightarrow \text{bpy}(\pi^*)$ T_1 state with $\tau = 250$ ps; the population of both states is independent of excitation wavelength in 6. This work demonstrates that the introduction of one NHC-R ligand in these complexes permits the population of a higher energy triplet state that decays to T_1 in the picosecond time range. The relatively slow $\text{T}_n \rightarrow \text{T}_1$ internal conversion in these complexes violates Kasha's Law, making the population of the higher-energy state potentially useful for more efficient charge injection into semiconductors for solar energy conversion or to aid in the population of dissociative metal-centered states for drug delivery. Overall, this work shows the ability to synthetically access valuable excited-state dynamics using the two different Ru-C bonds of the asymmetric NHC-R ligands.



INTRODUCTION

The excited states of ruthenium polypyridyl complexes have been used extensively in many applications, including photoelectrosynthesis cells,^{1,2} dye-sensitized solar cells,^{3–6} DNA intercalation and sensing,⁷ electron transfer reagents,⁸ photon upconversion,^{9,10} release of drug molecules,¹¹ photostability,¹² sensing,¹³ optoelectronics,¹⁴ and catalysis,¹⁵ among others.^{16–19} Because of the wide range of uses, there has been great interest in understanding and controlling the excited states of $\text{Ru}(\text{II})$ complexes to improve their properties, including lifetime, reactivity, and excitation energy. For example, the steric bulk and bite angle have been shown to have a pronounced effect on the excited-state reactivity and lifetime in $\text{Ru}(\text{II})$ complexes,^{20,21} and the replacement of nitrogen atoms by isoelectronic carbon,²² as well as the use of N-heterocyclic carbenes result in marked changes to the excited-state parentage and dynamics.^{23,24} The desirable

properties of $\text{Ru}(\text{II})$ complexes can vary from one application to another, such as the requirement of low-lying dissociative metal centered (${}^3\text{MC}$) states for drug release.^{25,26} In contrast, higher energy ${}^3\text{MC}$ states are required to attain longer lifetimes of the lowest energy metal-to-ligand charge transfer (${}^3\text{MLCT}$) excited state useful for solar energy conversion, sensing, and photoredox catalysis.^{27–29} One particular property that may be useful for both areas, enhanced charge injection into semiconductors and increased population of the ${}^3\text{MC}$ state(s) for drug release, is the presence of a ${}^3\text{MLCT}$ state at higher energy that is sufficiently long-lived to afford reactivity.

The Strassner group recently reported cyclometalated ruthenium(II) complexes where there are two Ru-C bonds, 62

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one from a N-heterocyclic carbene and one from a carbanion.³⁰ The Nazeeruddin group then introduced a series of electron-donating and -withdrawing groups on the cyclometallating ligand and showed the profound effect of the substituents on the electrochemistry and on the localization of the frontier molecular orbitals (MOs) on the molecule,³¹ highlighting that the properties of the NHC/carbanion ligand predominantly affect the highest occupied molecular orbital (HOMO) of the molecule, whereas the supporting polypyridyl ligands predominantly affect the lowest unoccupied molecular orbital (LUMO). While the electrochemistry and calculations examined the ground-state molecular orbitals, the excited-state properties of these complexes were not investigated.

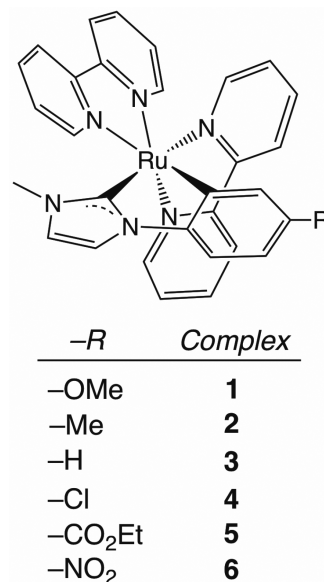
The related cyclometallating ligand 2-phenylpyridine (ppy) was shown to be successful in promoting hole injection from a [Ru(bpy)₂(ppy)]⁺ derivative to a p-type semiconductor, NiO.³² This hole injection is afforded by the covalency between the Ru–C bond of the ppy ligand, such that the HOMO exhibits significant ppy ligand character, resulting in a lowest energy triplet excited state that is Ru(d)/ppy(π) $\rightarrow$ bpy(π^*) in character, or meta/ligand-to-ligand charge transfer (³ML-LCT). The delocalization of charge onto the ppy ligand permits efficient hole injection following excitation due to the close spatial proximity between the Ru(d)/ppy(π) HOMO and the semiconductor when the ppy ligand is bound to NiO. We hypothesized that the NHC ligands, which bear not only the cyclometallating phenyl group of ppy, but also a highly σ -donating carbene lone pair for metal coordination, may exhibit improved excited-state properties as compared to [Ru(bpy)₂(ppy)]⁺ for hole injection applications. Importantly, the asymmetry of the NHC ligands is expected to further split the Ru–NHC t_{2g}-type occupied MOs, thus generating two low-lying ³ML-LCT states.

The present work focuses on the excited-state properties of six complexes with the general formula [Ru(bpy)₂(NHC-R)][PF₆], where bpy = 2,2'-bipyridine and NHC-R represent an N-heterocyclic carbene covalently bound to a deprotonated phenyl ring with a substituent –R positioned *para* to the NHC moiety. In the Ru(bpy)₂(NHC-R)[PF₆] series, R = –OMe (1), –Me (2), –H (3), –Cl (4), –CO₂Et (5), and –NO₂ (6), as depicted in Scheme 1. The Hammett parameters (σ_p^+) of the NHC-R ligands in 1–6 vary widely from –0.78 to 0.79 and range from electron-donating to electron-withdrawing. Complexes 1–6 exhibit extensive mixing of Ru and the NHC-R ligand in the HOMO. Two low-lying triplet excited states, T_n and T₁, are observed, both of which exhibit sufficiently long lifetimes to afford hole injection into NiO. While two independent low-lying ³MLCT states have been previously observed for Ru(II) complexes,^{33,34} to the best of our knowledge, this represents the first report of the population of two triplet states with sufficiently slow T_n $\rightarrow$ T₁ internal conversion in a cyclometalated or in a carbene complex to afford reactivity from both states.

EXPERIMENTAL SECTION

Materials. The synthesis of complexes 1,³⁰ 3,^{4,30} and 6³⁰ was accomplished following methods previously described, while 2, 4, and 5 were prepared using modified versions of the same published routes. The syntheses of the NHC-R ligands for 2,³⁵ 4,³⁶ and 5³⁷ have been previously described. The solvents, as well as 2,2'-bipyridine, ammonium hexafluorophosphate, tetra-*n*-butyl ammonium hexafluorophosphate, and cesium carbonate, were purchased from Sigma-Aldrich. The

Scheme 1. Schematic Representation of the Molecular Structures of 1–6



details of the synthesis are described in the Supporting Information and shown in Scheme S1 along with NMR and mass spectrometry data in Figures S1–S10.

Instrumentation and Methods. ¹H NMR spectra were obtained on a either a 400 or a 250 MHz Bruker DPX spectrometer (as noted in the Supporting Information) and referenced to the residual solvent peaks, 7.26 ppm for CDCl₃-d₁ and 1.94 ppm for CD₃CN-d₃.³⁸ Electrospray ionization was performed on a Bruker MicrOTOF mass spectrometer, and samples were dissolved in acetonitrile and standardized with sodium formate in water. Steady-state UV–vis electronic absorption data were collected on an Agilent Cary 8453 diode array spectrometer with a 1 cm × 1 cm quartz cuvette equipped with a gastight Kontes screwtop. Emission data were recorded on a FluoroMax-4 spectrofluorimeter (Horiba Jobin Yvon) in CH₃CN, and samples were deaerated by sparging with nitrogen for 15 min. The solutions were loaded into J-Young tubes and cooled with liquid nitrogen. Steady-state infrared absorption data were measured on a Spectrum 65 FT-IR spectrometer by PerkinElmer. The sample was contained within an airtight Herrick sample cell equipped with two 1 mm CaF₂ plates and a 0.1 mm spacer.

Time-resolved femtosecond transient absorption (fsTA) spectroscopy data were collected on a system that was previously described in detail.³⁹ Briefly, an Astrella laser system (Coherent) is used to provide an 800 nm pulse (8 mJ, 1 kHz rep. rate, ~35 fs pulse width). The Ti:Saph output was split to serve as the pump beam (3 mJ) and the remainder as the probe pulse. The excitation pulses pump an optical parametric amplifier (Coherent OPerA Solo), and the output was directed through an optical delay line (maximum delay of 4 ns) and attenuated to 2 μJ. All samples were at a concentration that afforded an absorption of ~0.3–0.5 at the sample excitation wavelength. A supercontinuum of white light was generated by focusing a portion of the remaining 800 nm beam onto a CaF₂ window on a rotating mount. The resulting light was dispersed on a Triax 550 spectrograph before being detected by a PIXIS CCD camera (Princeton Instruments) run using a home-built LabView program. The temporal resolution

164 or instrument response function (irf) was 85 fs determined
165 from the measurement of the optical Kerr effect in cyclo-
166 hexane. The samples were flowed in a Herrick Scientific flow
167 cell, which features two 1 mm CaF_2 plates with a 1 mm spacer.
168 Femtosecond time-resolved infrared spectroscopy (TRIR)
169 was also conducted on an instrument previously described in
170 detail.⁴⁰ Briefly, a Legend (Coherent) was seeded by a Mantis
171 (Coherent) short pulse oscillator with 800 nm output (2.4 mJ,
172 1 kHz rep. rate), and the output was split and directed into two
173 different optical parametric amplifiers (OPerA, Coherent).
174 One of the OPerA outputs was passed through an optical delay
175 line and served as the pump (maximum delay of 3 ns), while
176 the other was equipped with a difference frequency generation
177 module, which created the mid-IR continuum and served as
178 the probe beam. The sample cell used for TRIR was the same
179 as that for the steady-state IR experiments, and the absorption
180 of each sample at the pump wavelength was adjusted to be
181 between 0.5–0.8. The mid-IR light was dispersed by a Triax
182 320 spectrograph and detected using a HgCdTe CCD chip (32
183 $\times$ 2 pixels) with $\sim 4 \text{ cm}^{-1}$ resolution (InfraRed Associates
184 Inc.). The 180 fs time resolution was determined by measuring
185 the growth of the ³MLCT signature of $[\text{Ru}(\text{bpy})_3][\text{PF}_6]_2$.⁴¹

186 The electronic absorption spectrum of each sample was
187 measured before and after each time-resolved experiment to
188 ensure that no sample degradation had taken place. Addition-
189 ally, for all femtosecond time scale measurements, the pump
190 beams were passed through a linear polarizer set to the magic
191 angle of between the probe and pump beams to minimize the
192 measurements of anisotropy.⁴² All kinetic traces from fsTA and
193 TRIR were plotted and fitted using the Igor Pro software
194 (version 6.3.4.1) with a sum of exponential equations.

195 Transient absorption spectroscopy in the nanosecond time
196 scale (nsTA) was performed on an instrument previously
197 described.⁴³ Briefly, an Edinburgh LP980 spectrometer
198 equipped with single-wavelength photomultiplier tube detector
199 and an intensified CCD camera was used for broadband
200 measurement. The third harmonic of a Spectra-Physics INDI-
201 40 Nd:YAG laser (100 mJ/pulse, 10 Hz rep. rate) was focused
202 onto a Spectra-Physics Basican optical parametric oscillator to
203 produce the wavelengths of light used for excitation, attenuated
204 to ~ 6 –8 mJ/pulse for the experiments. The samples were
205 deaerated and loaded into the cells used for steady-state
206 electronic absorption at an absorption of ~ 0.3 at the excitation
207 wavelength.

208 Cyclic voltammograms (CVs) were recorded under a N_2
209 atmosphere using a BASi CV-50W (Bioanalytical Systems Inc.)
210 potentiostat. The cell consisted of a three-electrode arrange-
211 ment with a glassy carbon disc working electrode, a Ag/AgCl
212 aqueous working electrode (3 M NaCl), and a platinum coil
213 counter-electrode. All CVs were measured at a 20 mV/s scan
214 rate in CH_3CN with 0.1 M tetra- n -BuNPF₆ as the electrolyte
215 and referenced to the $\text{Fc}^{+/0}$ couple ($E_{1/2} = +0.382 \text{ V}$ vs SCE)
216 by adding ferrocene to the sample cell following each
217 experiment.⁴⁴ The same potentiostat and reference electrode
218 were used for the spectroelectrochemical measurements, with a
219 glassy carbon rod as the working electrode and a carbon fiber
220 mesh as the counter-electrode to increase the surface area in
221 contact with the solution. The two-compartment cell was
222 connected by a porous frit and continuously bubbled with
223 nitrogen, and the transmission side was fabricated using a 1 $\times$
224 1 cm quartz cuvette. The potentials of 1–5 were held 200 mV
225 more positive than the oxidation $E_{1/2}$ and 200 mV more
226 negative than the reduction $E_{1/2}$ to record the absorption

spectra of the one-electron oxidized and reduced species, 227
respectively. Complex 6 was held at 100 mV past the reduction 228
potential to prevent overlap with the second reduction peak. 229
The potentials were held until the current flow decreased by 230
95% of the initial value. 231

A Bruker D8 Venture Photon II with CPAD was used to 232
collect the single-crystal X-ray diffraction data for all four 233
complexes. The crystals were cooled with a stream of cold N_2 234
to 150 K with an Oxford Cryosystems Cryostream Cooler. 235
These structures were then solved using the OLEX program 236
with a plugin using the SHELXT program, which used an 237
intrinsic phasing solution method.^{2,45,46} The resulting data 238
were processed using SHELXL, which used a full-matrix least- 239
squares/difference Fourier cycle treatment for refinements.⁴⁷ 240
All non-hydrogen atoms were refined with anisotropic 241
displacement parameters. Most hydrogen atoms were placed 242
in ideal positions and refined as riding atoms with relative 243
isotropic displacement parameters, but in some instances using 244
the residual electron density map to assign hydrogen peaks 245
gave significantly better results. These hydrogen atoms are 246
identified and additional information is provided in the 247
Supporting Information. 248

Complexes 3 and 6 have been previously characterized by 249
single-crystal X-ray crystallography.^{30,31} Although 1 was 250
reported previously, it was not characterized crystallographi- 251
cally, and 2, 4, and 5 are new molecules. All of crystallographic 252
data for these complexes are provided in the Supporting 253
Information. Crystals for 1 and 2 were grown with the slow 254
diffusion of hexanes into a concentrated solution of acetone, 255
and those of 4 and 5 were grown in an analogous manner but 256
with acetonitrile and diethyl ether. For the crystal structure of 257
5, there was a large solvent channel that was the approximate 258
length of two diethyl ether molecules. As such, we attempted 259
to model the channel with two Et_2O molecules, both with 260
positional disorder over multiple positions, but this resulted 261
in a poor fit. These solvent molecules were removed using 262
PLATON, function: SQUEEZE, which resulted in the removal 263
of 144 electrons and a 479 $\text{\AA}^3$ solvent-accessible void per cell 264
(consistent with two diethyl ether molecules). For complexes 4 265
and 5, one PF_6^- counteranion in each structure exhibited 266
positional disorder. These were modeled by splitting the 267
disordered atoms into groups (PART instruction), moving the 268
atoms to the expected positions on the basis of residual 269
electron density, and allowing the atoms to refine freely. This 270
method was also used to model the positional disorder in 1 271
and 2 for the acetone molecules present in the crystal 272
structures. 273

All computational results were obtained using the Gaussian 274
09 suite of programs.⁴⁸ For geometry optimization and 275
frequency calculations (both singlet and triplet), the PBE 276
hybrid functional was used as it resulted in the best match with 277
experimental data.⁴⁹ The frequency calculations confirmed that 278
the calculated structures were at a local minima. For time- 279
dependent DFT,⁵⁰ the B3LYP functional was found to best 280
reproduce the experimental data.⁵¹ For all calculations, the 281
def2-TZVP basis set^{52,53} was used for all atoms^{4,41} with the 282
exception of ruthenium where the use of SDD ab initio 283
pseudopotentials was employed.^{54,55} All of the calculations 284
were undertaken using a Polarizable Continuum Model 285
(PCM)⁵⁶ with CH_3CN as the solvent. Natural bonding orbital 286
(NBO) calculations were undertaken to quantify the 287
percentage contribution of ruthenium-based orbitals to 288
molecular orbitals.⁵⁷ 289

RESULTS AND DISCUSSION

Synthesis and Single-Crystal X-ray Crystallographic

Characterization. Complexes 1, 3, and 6 were previously synthesized following the steps depicted in Scheme S1,^{30,31} whereas 2, 4, and 5 were new and were prepared following an analogous procedure. Complexes 1–6 were recrystallized from slow diffusion of diethyl ether into a concentrated acetonitrile solution, and the single-crystal X-ray diffraction structures of 1, 2, 4, and 5 are shown in Figure 1. There is very little

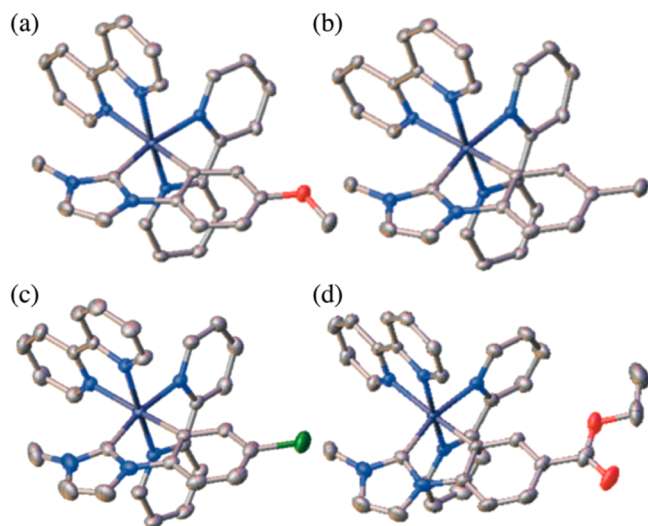


Figure 1. Thermal ellipsoid plots of (a) 1, (b) 2, (c) 4, and (d) 5 shown at 50% probability (gray = carbon, blue = nitrogen, red = oxygen, green = chlorine, and dark blue = ruthenium); crystallized solvent molecules, counteranions, and hydrogens are omitted for clarity.

perturbation across the four complexes in the $\sim 101^\circ$ C–Ru–C angles, with the largest difference of 0.5° , or in the Ru–C distances, where the largest difference is 0.02 Å. The Ru–C distances in 1, 2, 4, and 5 are comparable to those reported for $[\text{Ru}(\text{bpy})_2(\text{ppy})]^+$ and related cyclometalated complexes, which feature bond lengths in the 1.99 – 2.08 Å range.⁵⁸ The atomic coordinates and crystallographic details specific to each crystal are summarized in Tables S1–S8.

Electronic Absorption, Emission, and Electrochemis-

try. The room-temperature electronic absorption and 77 K emission spectra of 1–6 in CH_3CN are shown in Figure 2, and

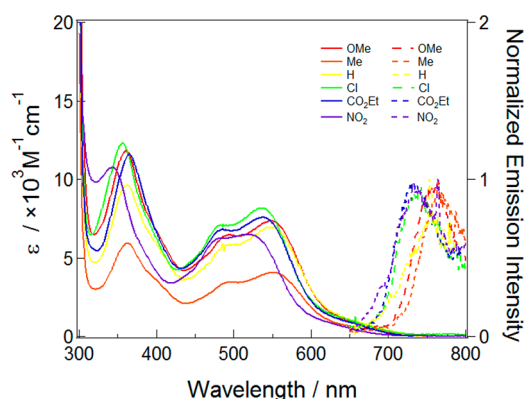


Figure 2. Electronic absorption (solid lines, 298 K) and emission (dashed lines, $\lambda_{\text{exc}} = 540$ nm, 77 K) of 1–6 in CH_3CN .

relevant data are summarized in Table 1. Complex 1 exhibits a ligand-centered $^1\pi\pi^*$ transition associated with the NHC-OMe

Table 1. Electronic Absorption Maxima, λ_{abs} , Molar Extinction Coefficients, ϵ , and Electrochemical Reduction Potentials, $E_{1/2}$, for 1–6 in CH_3CN

complex	$\lambda_{\text{abs}}/\text{nm}$ ($\epsilon/\times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	$E_{1/2}/\text{V}^a$
1	360 (12), 494 (6.5), 548 (7.4)	−1.50, +0.50
2	363 (5.9), 492 (3.4), 550 (4.1)	−1.48, +0.51
3	363 (9.6), 488 (5.5), 547 (7.0)	−1.49, +0.52
4	357 (12), 485 (7.0), 537 (8.2)	−1.48, +0.60
5	364 (12), 486 (6.9), 539 (7.6)	−1.49, +0.58
6	344 (11), 482 (6.2), 519 (6.5)	−1.52, −1.34, −1.12, +0.69

^a0.1 M Bu_4NPF_6 ; vs Ag/AgCl.

ligand at 360 nm and two singlet metal/ligand-to-ligand charge transfer ($^1\text{ML-LCT}$) bands with maxima at 493 and 549 nm; the latter tails from ~ 620 to ~ 750 nm. Complexes 2–6 exhibit similar features that resemble the electronic absorption spectrum of $[\text{Ru}(\text{bpy})_2(\text{ppy})]^+$, with maxima at 365, 402, 486, and 543 nm in methanol.⁵⁹ The series features a bathochromic shift of the $^1\text{ML-LCT}$ peaks from 6 at 519 nm to 1 at 548 nm as the NHC-R ligand becomes more electron-donating, making the Ru(II) center easier to oxidize.

As shown in Figure 2, 1 emits light with maximum at 763 nm ($\lambda_{\text{exc}} = 540$ nm) in CH_3CN at 77 K with a large Stokes shift (5060 cm^{-1}) from the lowest energy $^1\text{ML-LCT}$ peak at 549 nm, consistent with the luminescence of related Ru(II) complexes.^{60,61} Similar phosphorescence is observed for 2–6 at 77 K (Figure 2). These features are common among all six complexes; the maxima of 1–3 appear at roughly the same energy, ~ 760 nm, and those of 4–6 at ~ 735 nm. Emission at room temperature was not detected for 1–6 in CH_3CN . The low emission is in contrast to $[\text{Ru}(\text{bpy})_3]^{2+}$, which absorbs at 452 nm and emits at room temperature ($\lambda_{\text{em}} = 620$ nm). It is expected that the increase in σ -donating ability of the NHC-R ligand should result in an increase in energy of the metal-centered highest occupied molecular orbital (HOMO), thus lowering the energy required to promote an electron into the $\text{bpy}(\pi^*)$ LUMO. This red shift in the absorption observed for 1–6 is also present in $[\text{Ru}(\text{bpy})_2(\text{ppy})]^+$ relative to that of $[\text{Ru}(\text{bpy})_3]^{2+}$.

The electrochemistry of 1–6 was examined in acetonitrile, and the results are shown in Figure 3 and summarized in Table 1. The first oxidation of 1 is observed at $E_{1/2} = +0.50$ V vs Ag/AgCl in CH_3CN , and it shifts to more positive potentials with increasing electron-withdrawing ability of the substituent on the NHC-R ligand; the magnitude of the difference between the first oxidation in 1 and 6 is 190 mV, and that between 3 and 6 is 170 mV. This couple is assigned to a metal-centered oxidation, and the shift is comparable to that measured for $[\text{Ru}(\text{bpy})_2(\text{ppy})]^+$ and $[\text{Ru}(\text{bpy})_2(\text{NO}_2\text{-ppy})]^+$, where $\text{NO}_2\text{-ppy}$ is a NO_2 -substituted phenylpyridine, +120 mV.⁵⁸ For complexes 1–5, the first reduction couple is essentially unchanged, within ~ 20 mV, and is assigned to the reduction of the bpy ligand. Similar complexes with only bpy ligands feature their first ligand reductions at roughly this potential.^{63–65} However, 6 exhibits a positive shift of 380 mV attributed to the stabilization of the π^* orbital of the NHC- NO_2 /carbanion orbital by the presence of the strong electron-withdrawing group.

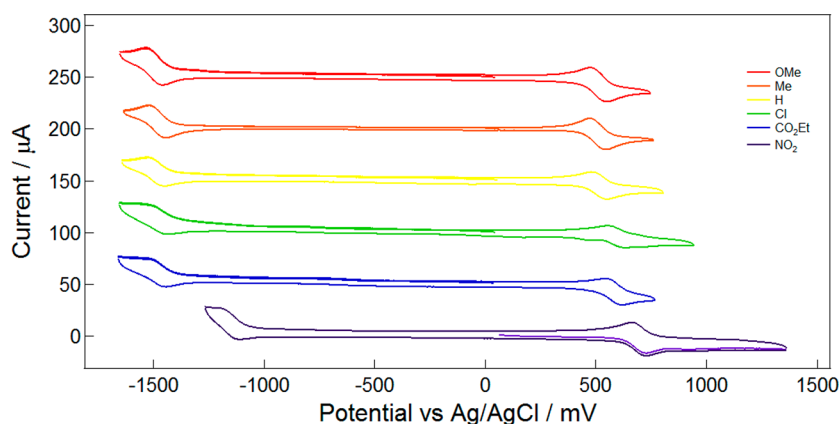


Figure 3. Cyclic voltammograms of 1–6 recorded in CH₃CN (0.1 M ⁿBu₄NPF₆ electrolyte; each trace above complex 6 is offset by 50 μA for clarity).

Density Functional Theory Calculations. The calculated molecular orbital (MO) diagrams of 1–6 are shown in Figure 4, which display a clear trend in the energy of the HOMO

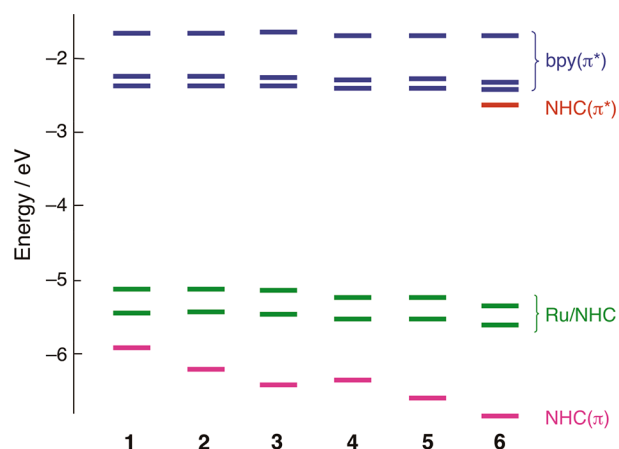


Figure 4. Ground-state singlet molecular orbital diagrams for 1–6.

across the series. The HOMO of the complex with the most electron-donating NHC-R ligand (R = –OMe), 1, is slightly destabilized as compared to that with a –H substituent, 3. The opposite trend is calculated for 6, where the HOMO is stabilized relatively those of 1–5. The calculated HOMO energy difference of 0.24 eV from 1–6 is in reasonably good agreement with the electrochemistry data, which show a total shift in the first oxidation couple of 0.19 V from 1 to 6. The calculated energies of the LUMOs of 1–5 are also in good agreement with the electrochemical data, with only a small difference of <30 meV among the five complexes and consistent with an MO centered on a bpy(π*) orbital. In contrast, a large difference in the energy of the LUMO is calculated for 6, 220 meV, as compared to the next closest in value, 5. This finding is consistent with the electrochemistry and also with the calculated localization of the LUMO on the NHC-NO₂(π*) orbital positioned at a lower energy than the bpy(π*) MOs (Figure 4).

The absorption data generally agree with the trends found in the DFT and TD-DFT calculations (Tables S9–S14). The electron-donating NHC–OMe ligand in 1 raises the energy of the HOMO as compared to the rest of the series, resulting in a smaller HOMO–LUMO gap reflected in the red-shifted

lowest energy absorption maximum for this complex. The tails of absorption are difficult to compare due to their low intensity, but these too appear to agree with the calculated values, because those of complexes with more electron-donating ligands extend further into the red wavelengths and with a higher intensity as compared to those with electron-withdrawing groups.

The electron densities of the frontier molecular orbitals of 1–5 are similar and exemplified in the electron density plots shown in Figure 5 for 2. The contribution from the

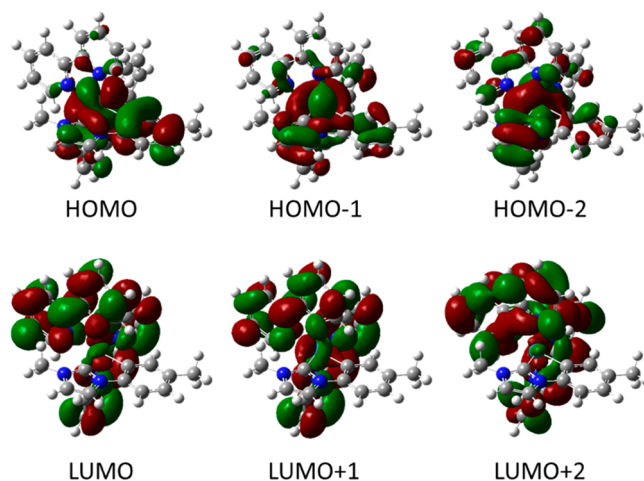


Figure 5. Electron density plots of the frontier MOs of 2 (drawn at isovalue = 0.02).

cyclometallating ligand is clearly evident in the HOMO, HOMO–1, and HOMO–2 of 2. In contrast, the LUMO, LUMO+1, and LUMO+2 of 2 exhibit nearly no contribution from the NHC/carbanion ligand, with the majority of the electron density residing on the bpy ligands. In complex 6, the LUMO is NHC-NO₂(π*) in character below the bpy(π*) orbitals. The electron density of the LUMO of 6 is depicted in Figure S15. These trends are consistent with the NBO calculation results, summarized in Tables S15 and S16, where a greater contribution to the HOMO is calculated for the more electron-donating ligands, as evidenced by a decrease in total Ru contribution.

The TD-DFT calculations predict a large number of low oscillator strength bands at lower energies for 1–6, the lowest

of which arises primarily from the HOMO $\rightarrow$ LUMO transition. Together with the experimental data and comparisons to related complexes, the computational results lead to an assignment of the lowest energy absorption in 1–5 as arising from the population of the lowest energy singlet, $^1\text{ES}_1$, associated with a Ru(d)/NHC(π) $\rightarrow$ bpy(π^*) transition of $^1\text{ML-LCT}$ character, and a ligand-centered Ru(d)/NHC(π) $\rightarrow$ NHC(π^*) transition for 6. The singlet excited states immediately above $^1\text{ES}_1$, $^1\text{ES}_2$ – $^1\text{ES}_4$, are calculated to possess relatively low oscillator strengths, with the next transition with significant intensity predicted to be to $^1\text{ES}_5$, and primarily composed of electron density movement from the HOMO–1 and HOMO–2 to the LUMO+1 and LUMO+2. The HOMO–1 and HOMO–2 are localized on the NHC-R ligand and the Ru metal, but possess significantly smaller contribution from the carbanion ring as compared to the HOMO. The $^1\text{GS}_1 \rightarrow ^1\text{ES}_5$ transition is predicted at 519 nm in 1 and is calculated to progressively shift to higher energy across the series to 507 nm in 5. These results are in qualitative agreement with the electronic absorption data for the complexes in Figure 2 and Table 1. The lowest energy triplet excited state of each of 1–6 is predicted to be $^3\text{ML-LCT}$ in nature (Figures S16–S20).

Spectroelectrochemistry and Nanosecond Transient Absorption. The spectroelectrochemistry of 1–6 was utilized to aid in the interpretation of the transient absorption data. Upon oxidation of 1–6, a decrease in the absorption in the 400–600 nm range is observed, along with a broad increase in intensity at ~ 600 nm. In similar Ru(III) polypyridyl complexes, the absorption at long wavelengths has been previously attributed to ligand-to-metal charge transfer (LMCT) transitions from ligand(π) to Ru $^{3+}$ (d) orbitals, while the decrease in ground-state absorption is associated with a shift in the MLCT transition to higher energies outside the measurement window.^{41,66,67} The difference spectra collected upon one-electron reduction are similar for 1–5, but substantially different for complex 6, as expected from the electrochemistry and DFT calculations. Reduction of 1–5 results in an increased absorption in the UV and near-UV regions, indicating the presence of a reduced bpy ligand,⁶⁸ whereas in the case of 6, the one-electron reduced complex absorbs strongly from 350–450 nm and beyond 550 nm (Figure S25). These features are attributed to the reduction of the NHC/carbanion ligand rather than the modest increases in the UV region typical of bpy radical anions. These changes are exemplified in difference absorption plots in Figure 6a for the oxidation and reduction of 5.

The nanosecond transient absorption spectra of 1–5 exhibit broadband absorption profiles that bear a striking resemblance to the spectroelectrochemistry data, as shown in Figure 6b for 5. A ground-state bleach is observed in 1–5 between 400–600 nm, and broad positive absorption features at $\lambda < 400$ nm and between 600 and 800 nm, consistent with a $^3\text{ML-LCT}$ excited state. In general, the decays of both the positive signal and the bleach can be fitted to a monoexponential function consistent with the relaxation of the $^3\text{ML-LCT}$ excited state to the ground state with $\tau = 15 \pm 0.1$ ns (Table 2). The instrument response function (irf) of the instrument is ~ 8 ns, and the lifetimes, τ , of some of the complexes cannot be accurately deconvoluted from the irf; in fact, 1–6 exhibit $\tau < 20$ ns at room temperature and are summarized in Table 2. As expected, extension of the $^3\text{ML-LCT}$ lifetimes was observed for 1–6 at 77 K, and the results are listed in Table 2 for 1–5. On this instrument, the

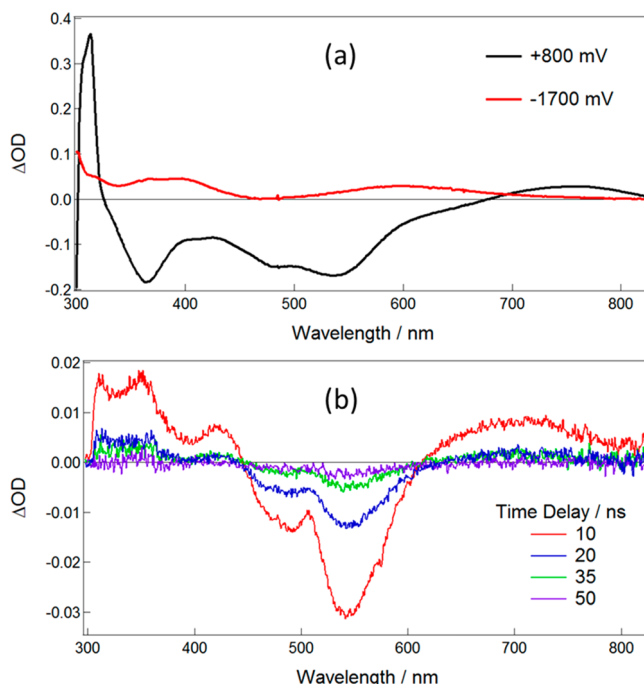


Figure 6. Difference spectra of 5 (a) recorded after electrochemical oxidation and reduction at +0.8 and –1.7 V vs Ag/AgCl, respectively, and (b) collected at various times following a 550 nm excitation (irf ~ 6 ns) in deaerated CH_3CN .

Table 2. Excited-State Lifetimes of 1–5 in CH_3CN

complex	τ/ps^a	τ/ns^c	τ/ns^d
1	7 ± 2	3–8	10.1 ± 0.1
2	9 ± 1	3–8	10.1 ± 0.3
3	10 ± 3^b	8.7 ± 0.3	11.3 ± 0.3
4	16 ± 2	15.9 ± 0.1	16.2 ± 0.1
5	22 ± 3^b	15.2 ± 0.1	23.0 ± 0.1

^aA long-lived component with $\tau > 3$ ns was observed for 1–5; $\lambda_{\text{exc}} = 400$ nm, irf ~ 85 fs. ^bA < 1.0 ps vibrational cooling component was observed. ^c $\lambda_{\text{exc}} = 550$ – 670 nm, 298 K, irf ~ 8 ns. ^d $\lambda_{\text{exc}} = 550$ nm, 77 K, irf ~ 8 ns, fit to the decay of emission.

lifetime of 6 at 298 K was too short to be observed, but was measured to be 9.9 ± 0.1 ns at 77 K in CH_3CN ($\lambda_{\text{exc}} = 550$ nm).

Femtosecond Transient Absorption and Time-Resolved IR (TRIR) Spectroscopies. To elucidate the excited-state dynamics of 1–6, each of the complexes was examined using pump–probe spectroscopy on the femtosecond time scale. When complex 1 is excited in the 550–670 nm range, a large ground-state bleach between 450 and 600 nm develops within the laser pulse (Figures 7 and S24). Additionally, a small but persistent excited-state absorption is observed at wavelengths > 600 nm, consistent with a $^3\text{ML-LCT}$ excited state. With these low energy excitation wavelengths, only a vibrational cooling component is observed along with signal that does not decay within the 3 ns maximum time scale of measurement. Similar spectral and decay profiles were collected for 2–5 (Figures S25–S29), and these results are consistent with the > 3 ns lifetimes observed using nanosecond excitation (Table 2).

With 400 nm excitation, higher energy excited states are accessed, leading to an additional component in the picosecond time range for 1–5 as summarized in Table 2 and

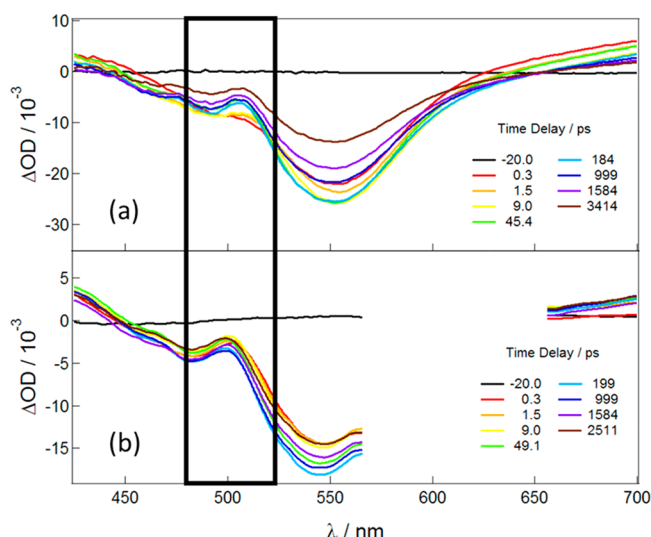


Figure 7. Transient absorption spectra of **1** in CH_3CN at various delay times following (a) 400 nm and (b) 620 nm excitation (irf = 85 fs). The black box highlights the spectral differences between the two excitation wavelengths.

exemplified in Figure 7a for **1**. This 7–22 ps component is evident in the growth of a feature at ~ 510 nm for **1–5** during this time range (Figure 7a for **1** and Figures S25–S29 for **2–5**). At longer wavelengths, a shift is also observed at roughly the same time scale. This shift and the spectral changes at ~ 510 nm are not observed with lower energy excitation of **1–5**.

In Ru(II) complexes, intersystem crossing (ISC) is known to proceed within ~ 40 fs,^{69,70} such that the differences observed with 400 nm and 550–670 nm excitation in the picosecond time scale must be taking place in the triplet manifold. In general, the spectral features of the 7–22 ps component in **1–5** are similar to those of the long-lived excited state with $\tau \geq 3$

ns, such that they can both be assigned as arising from $^3\text{ML-LCT}$ states. It may be hypothesized that ISC upon 400 nm excitation results in the initial population of a higher energy $^1\text{ML-LCT}$ state that intersystem crosses to a higher energy triplet $^3\text{ML-LCT}$ state, T_n , within the 85 fs laser pulse; the latter then decays to the lowest energy $^3\text{ML-LCT}$ state, T_1 , with time constants that range from 7–22 ps in **1–5** (Table 2). Population of the lowest energy $^1\text{ML-LCT}$ state of **1–5** with 550–670 nm excitation results in the observation of the $^3\text{ML-LCT}$ T_1 state, which decays to the ground state with lifetimes ≥ 3 ns, as listed in Table 2.

To gain further information on the population of the $^3\text{ML-LCT}$ T_n state, complex **1** was pumped using different wavelengths, 400, 550, 620, 640, and 670 nm; however, only 400 nm excitation gave rise to the 7 ps component (Figure 7a). There was not a substantial difference observed in the longer wavelength excitations. Complexes **2–5** were examined with a minimum of three pump wavelengths, 400, 550, and ~ 670 nm. Similar to the results for **1**, the component with lifetime in the 9–22 ps range was only observed with 400 nm, and there was no significant difference in band shape or lifetime between 550 nm and >650 nm.

In contrast to **1–5**, the transient absorption signals observed for **6** exhibit a biexponential decay regardless of excitation at high or low energy from 400 to 670 nm, with $\tau_1 = 90 \pm 30$ ps (47%) and $\tau_2 = 180 \pm 50$ ps (53%) in CH_3CN at 298 K ($\lambda_{\text{exc}} = 400$ nm, fit at 591 nm). From the calculations, the lowest energy singlet transition in **6** is predicted to be $^1\text{Ru(d)}/\text{NHC}(\pi) \rightarrow \text{NHC}(\pi^*)$ in nature, whereas the lowest energy minimized structure of the triplet state is $^3\text{Ru(d)}/\text{NHC}(\pi) \rightarrow \text{bpy}(\pi^*)$. As such, the transient absorption experiments can be explained by the initial population of the $^1\text{Ru(d)}/\text{NHC}(\pi) \rightarrow \text{NHC}(\pi^*)$ state upon absorption of a photon, followed by intersystem crossing to both a higher energy $^3\text{Ru(d)}/\text{NHC}(\pi) \rightarrow \text{NHC}(\pi^*)$ state, T_n , and the lowest energy $^3\text{Ru(d)}/\text{NHC}(\pi) \rightarrow \text{bpy}(\pi^*)$ state, T_1 . The assignment of both states

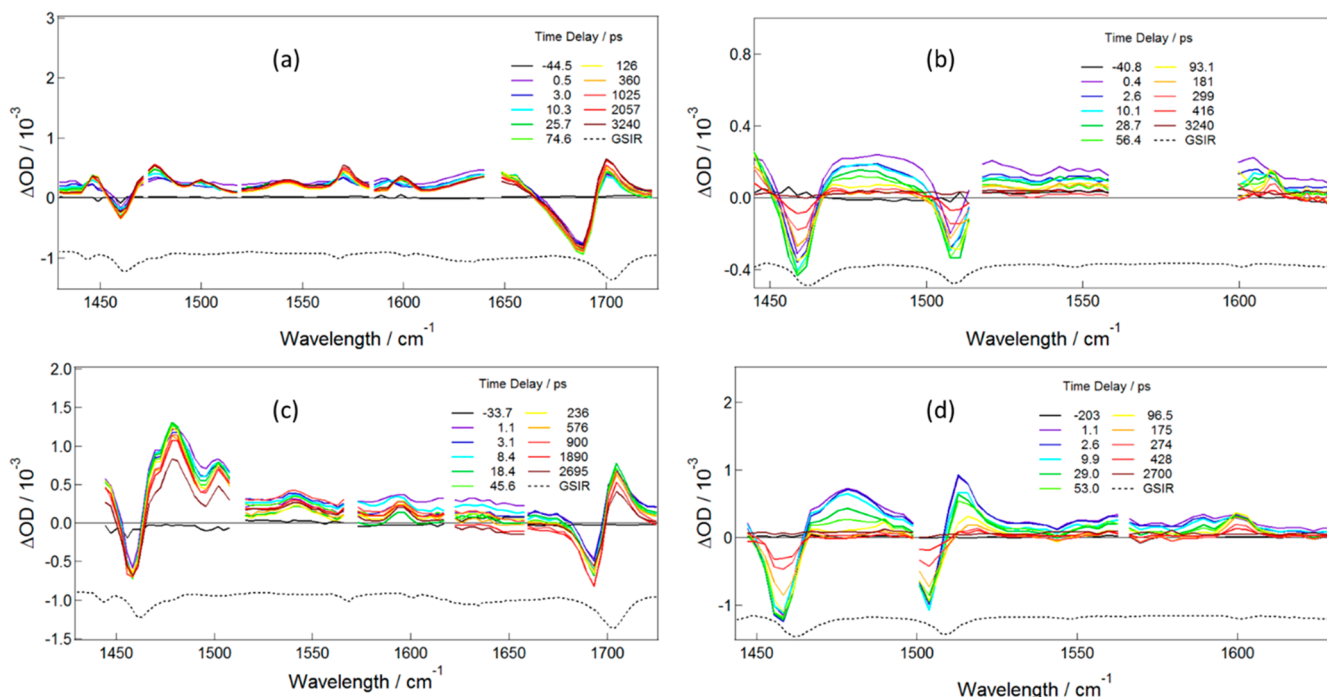


Figure 8. TRIR difference spectra in acetonitrile- d_3 of (a,c) **5** and (b,d) **6** with (a,b) $\lambda_{\text{exc}} = 400$ nm and (c,d) $\lambda_{\text{exc}} = 585$ nm (irf ~ 185 fs).

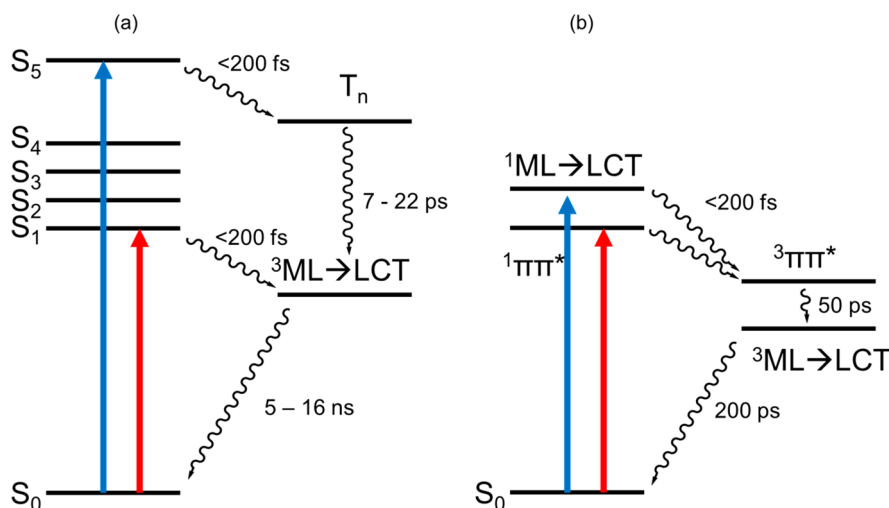


Figure 9. Jablonski diagrams of the excited-state processes in (a) 1–5 and (b) 6 where a Ru(d)/NHC(π) $\rightarrow$ NHC(π^*) state is denoted as $\pi\pi^*$ and a Ru(d)/NHC(π) $\rightarrow$ bpy(π^*) state is denoted as ML $\rightarrow$ LCT.

as $^3\text{ML-LCT}$ in 6 stems from the similarities to those of 1–5. Moreover, the $T_n \rightarrow T_1$ transition in 6 features changes at ~ 510 nm, as is also the case for 1–5.

To further examine the spectral features of the triplet T_n state of 1–6, TRIR spectroscopy was employed using multiple pump wavelengths in CD_3CN (irf ~ 185 fs). Complexes 5 and 6, which have IR specific markers, were examined in the ~ 1400 to ~ 1700 cm^{-1} range to capture any shifts of both of the ligand aromatic ring stretches and the IR active functional groups, whereas 1–4 were only monitored between ~ 1420 and 1550 cm^{-1} .

Each complex was excited with 400 nm pump light and a lower energy pump wavelength that corresponded to the red side of the absorption maximum (Figure 8 and Figures S30–S33). With higher energy excitation of 5, several features grow in over the course of 25 ps (Figure 8a). Most notably, a new peak develops at 1500 cm^{-1} , and the peak corresponding to the aromatic ring stretch at 1590 cm^{-1} shifts to higher energy by 10 cm^{-1} . The time scale of these changes, 22 ps, is consistent with the decay of the higher-energy $^3\text{ML-LCT}$ state, T_n , to T_1 measured by fsTA (Table 2). The changes are not consistent with vibrational relaxation usually observed in TRIR spectra, which are signified by the sharpening of peaks without significant shifting or growth. These changes are not observed in the spectra collected with a lower energy pump (Figure 8c), consistent with the absence of the picosecond decay for 1–5. When excited with shorter wavelength light, the observed shift of the aromatic peak to higher frequencies is explained by a loss of back-donation from the Ru(II) to π^* orbitals on the NHC ligand when the metal is oxidized in the charge transfer state.⁷¹ Notably, there is no shift in the CO_2Et IR handle at 1700 cm^{-1} , which reflects the lack of a rearrangement of electron density on that portion of the ligand. These observations parallel those measured in the transient absorption and point to a $T_n \rightarrow T_1$ internal conversion with time constant of 22–25 ps from a higher $^3\text{ML-LCT}$ state to the lowest $^3\text{ML-LCT}$ state. The kinetics of the $T_n \rightarrow T_1$ transition measured in the TRIR experiments are consistent with those recorded in the transient absorption measurements of 1–4 (Figures S20–S23).

Unlike 1–5, there are no differences upon excitation of 6 with 400 and 550 nm (Figure 8b and d). In each case, the

vibrational frequency of the $-\text{NO}_2$ group is observed to shift from 1595 cm^{-1} at early times to 1610 cm^{-1} at late times. The lifetime associated with this shift, 50 ± 20 ps, is consistent with the measured transient absorption data. The early time points of the spectra show the $-\text{NO}_2$ band at lower frequencies than the ground-state frequency (1602 cm^{-1}). This is consistent with a removal of electron density from a bonding orbital and placing it into an antibonding orbital as in a Ru(d)/NHC(π) $\rightarrow$ NHC(π^*) state. At later times, this band moves to higher frequencies, indicating an increased bond strength. The calculations predict that a higher stretching frequency would result in the $^3\text{Ru(d)/NHC}(\pi) \rightarrow \text{bpy}(\pi^*)$ excited state of 6 as compared to the ground state by ~ 7 cm^{-1} , which is consistent with the experimentally observed values. The TRIR of 6, as is also the case with the fsTA experiments, can be explained by the initial population of the $^1\text{Ru(d)/NHC}(\pi) \rightarrow \text{NHC}(\pi^*)$ state upon absorption of a photon, followed by intersystem crossing to both a higher energy $^3\text{Ru(d)/NHC}(\pi) \rightarrow \text{NHC}(\pi^*)$ state and the lowest energy $^3\text{Ru(d)/NHC}(\pi) \rightarrow \text{bpy}(\pi^*)$, T_1 .

These results show that the excitation of 1–5 with low energy light results in the population of the lowest energy $^1\text{ML-LCT}$ state, which directly converts to the lowest energy $^3\text{ML-LCT}$ state, T_1 , before returning to the ground state. With high energy light, the initial population of S_n affords intersystem crossing to T_n , which then undergoes internal conversion to the lowest energy $^3\text{ML-LCT}$ state, T_1 . This pathway is shown in Figure 9a, where the $T_n \rightarrow T_1$ internal conversion takes place with time constants of 7–22 ps in 1–5. In complex 6, both high- and low-energy excitation result in the initial population of the $^3\text{Ru(d)/NHC}(\pi) \rightarrow \text{NHC}(\pi^*)$ state, such that internal conversion in the triplet manifold is present and independent of excitation wavelength (Figure 9b).

Relationship of Hammett Parameter to Excited-State Deactivation.

The trend of the time constant of the $T_n \rightarrow T_1$ for 1–5 can be correlated to a Hammett parameter within the series. Complex 6 is excluded from this analysis because the excited-state dynamics likely involve $\pi\pi^*$ states, which are inaccessible to the other complexes. While this series is small, there is a clear trend that arises from the picosecond lifetimes measured in both the fsTA and the fsTRIR data. The more electron-donating substituents lead to a shorter initial lifetime, 624

625 7 ± 2 ps for $R = -\text{OMe}$ in **1**, and more electron-withdrawing
626 substituents lead to a longer lifetime, 22 ± 3 ps for $R =$
627 $-\text{CO}_2\text{Et}$ in **5**.

628 When fit to a Hammett parameter plot, the short lifetimes
629 measured from fsTA data fit best with the σ_p^+ *para* parameters
630 that have been optimized for electron donation into a π -
631 electron-accepting system (such as a Ru^{3+} center),⁷² as shown
632 in Figure 10 ($R^2 = 0.97$). The linear fit when using the σ_p^+

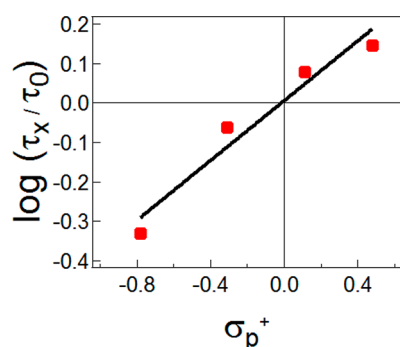


Figure 10. A Hammett parameter plot of the rates of internal conversion from $T_n \rightarrow T_1$ in **1**, **2**, **4**, and **5** as a function of σ_p^+ values, where τ_x is the lifetime of T_n for each complex and τ_0 is the lifetime of T_n for complex **3**.

633 parameters shows that the rearrangement of electron density
634 on the ruthenium center is not the primary effect that controls
635 the $T_n \rightarrow T_1$ rate constant, which is positioned meta to the
636 substituent R in NHC- R , and would result in a better fit with
637 σ_m values. Instead, the movement of electron density on the
638 NHC ligand appears to be more important in controlling this
639 process, where the substituent is *para* to the carbene-
640 containing NHC ring. While not conclusive by itself, this
641 analysis is consistent with the assignment of a T_n state that is
642 Ru^{3+} based, but with significant unpaired electron density in
643 the NHC/carbanion ligand in the $^3\text{ML-LCT}$ excited state(s).

644 CONCLUSION

645 The six ruthenium cyclometalated/carbene complexes of the
646 type $[\text{Ru}(\text{bpy})_2(\text{NHC-R})]^+$ exhibit low-energy light absorption
647 and have unique and controllable excited-state dynamics. In
648 each of the complexes, there are two low-energy triplet states
649 that are $\text{Ru}(\text{d})/\text{NHC}(\pi) \rightarrow \text{bpy}(\pi^*)$ $^3\text{ML-LCT}$ in nature. The
650 rate of internal conversion from the higher energy triplet, T_n ,
651 to T_1 is controlled by an easily modifiable substituent R on the
652 NHC- R ligand, which exhibits significant covalency to the
653 $\text{Ru}(\text{II})$ metal center. For each of the six complexes, the two
654 states, T_n and T_1 , are sufficiently long-lived to undergo charge
655 injection into a semiconductor following excitation with visible
656 light. Because the hole of the HOMO extends onto the
657 synthetically modifiable NHC- R ligand, these complexes have
658 the potential to be capable hole-injectors into p-type
659 semiconductors for use in solar energy conversion devices.
660 Using a Hammett parameter analysis, deeper understanding
661 into the nature of these excited states can be gained, and
662 general guiding principles for excited-state engineering in these
663 complexes are established. Importantly, the ability of the
664 NHC- R complexes to populate a higher energy excited state
665 with an appreciable lifetime provides a means to improve not
666 only charge injection but can also play a role in enhancing the
667 population of higher-lying metal-centered state(s) important
668 for photoinduced drug delivery.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the
ACS Publications website at DOI: 10.1021/acs.jpca.9b00858.

Synthetic schemes, characterization data, mass spec-
trometry, NMR, X-ray crystallography data, additional
DFT and TD-DFT information, and additional nsTA,
fsTA, fsTRIR, and spectroelectrochemistry spectra
(PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: turro.1@osu.edu.

ORCID

Claudia Turro: 0000-0003-3202-5870

Notes

The authors declare no competing financial interest.

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