



Title	[Ru(bpy)3]2+ analogues containing a N-heterocyclic carbene ligand
Authors(s)	Ghattas, Wadih, Müller-Bunz, Helge, Albrecht, Martin
Publication date	2010
Publication information	Ghattas, Wadih, Helge Müller-Bunz, and Martin Albrecht. "[Ru(Bpy)3]2+ Analogues Containing a N-Heterocyclic Carbene Ligand." ACS, 2010. https://doi.org/10.1021/om100925j .
Publisher	ACS
Item record/more information	http://hdl.handle.net/10197/3702
Publisher's statement	This document is the Accepted Manuscript version of a Published Work that appeared in final form in Organometallics, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see http://dx.doi.org/10.1021/om100925j
Publisher's version (DOI)	10.1021/om100925j

Downloaded 2026-05-01 23:33:58

The UCD community has made this article openly available. Please share how this access benefits you. Your story matters! (@ucd_oa)



© Some rights reserved. For more information

$[\text{Ru}(\text{bpy})_3]^{2+}$ analogues containing a N-heterocyclic carbene ligand

*Wadih Ghattas, Helge Müller-Bunz, and Martin Albrecht**

School of Chemistry & Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland

*To whom correspondence should be addressed. E-mail: martin.albrecht@ucd.ie; fax: +35-317162501

ABSTRACT

A synthetic procedure is described that provides access to $[\text{Ru}(\text{bpy})_3]^{2+}$ analogues in which one bpy ligand is replaced by a *C,N*-bidentate coordinating carbene-benzimidazole ligand (bpy = 2,2'-bipyridine). These new complexes were prepared by first installing the chelating carbene ligand onto a Ru(cymene) platform and subsequent ligand substitution using bpy or terpy (terpy = 2:2',6':2''-terpyridine). The carbene ligand significantly affects the optical properties of the complex and lowers the ruthenium(II) oxidation potential substantially. Such modifications may be advantageous for the development of new classes of photosensitizer materials.

Introduction

Ruthenium polypyridine complexes like $[\text{Ru}(\text{bpy})_3]^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine) and its derivatives have been extensively studied as active components in a variety of applications including supramolecular assembly, (photoinduced) electron-transfer reactions, and photochemistry.¹ In particular, this class of compounds show excellent properties as photosensitizers in dye-sensitized solar cells (DSSCs) and have thus been pivotal for advancing light-to-energy-conversion technology.² While substantial modifications in the polypyridine substitution pattern has been successfully applied as a methodology for improving the metal-centered redox and excited state properties,³ replacement of one or several pyridine ligand sites by N-heterocyclic carbenes (NHCs) has received surprisingly little attention. Tanaka and coworkers used mono-quaternized bpy and terpy analogues (terpy = 2:2',6':2''-terpyridine) to induce a mono-pyridylidene coordination mode of these ligands (**I** and **II**, Fig. 1),⁴ and Son *et al.* developed a procedure for the synthesis of homoleptic ruthenium(II) complexes containing *C,N*-bidentate carbene-pyridine and *C,N,C*-tridentate carbene-pyridine-carbene ligands, respectively (**III** and **IV**, Fig. 1).⁵ More recently, Hahn and coworkers succeeded in the preparation of bis(cyclometalated) systems of type **V**.⁶ The scarce appearance of NHC analogues of ruthenium polypyridine complexes is remarkable when considering that the strong donor properties of NHCs⁷ favorably affect the redox potential of coordinated metal centers,⁸ thus inducing useful properties for the fabrication of functional materials.⁹ Specifically, the stronger donor ability is expected to facilitate charge separation as required in solar cell active sites.

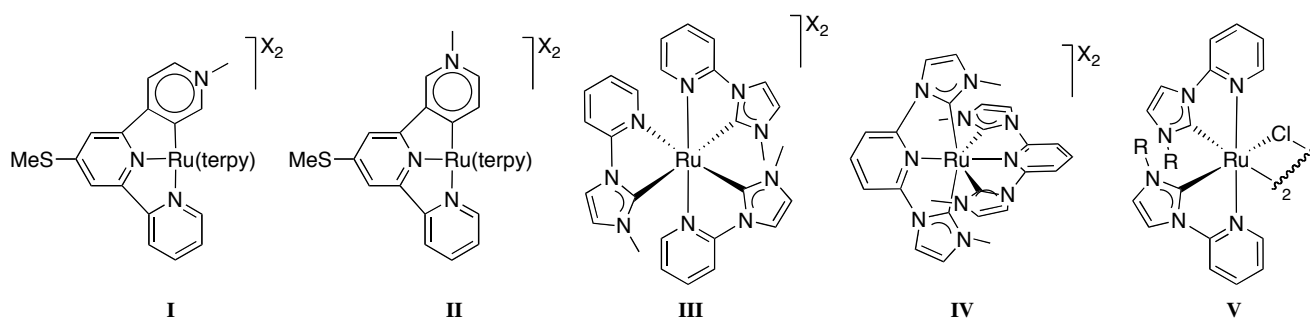


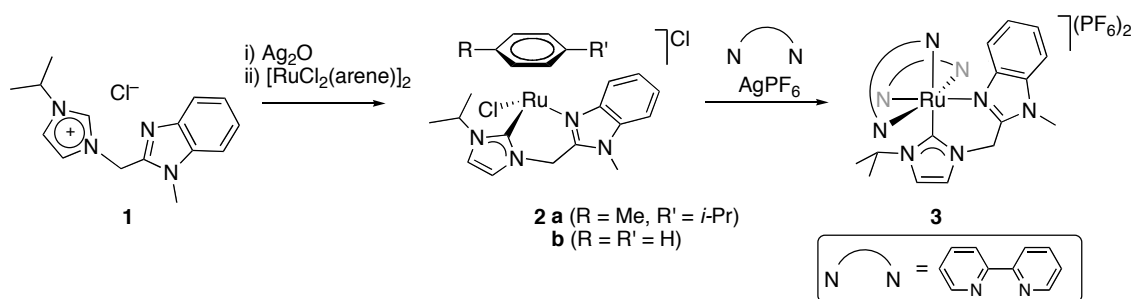
Figure 1. Known analogues of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{terpy})_2]^{2+}$ comprising N-heterocyclic carbene ligands ($X = \text{PF}_6$, $R = \text{Mes}$).

Here, we report on a convenient approach towards NHC ruthenium complexes comprising different ancillary polypyridine ligands such as bpy or terpy. This methodology is based on arene substitution from widely studied and readily accessible complexes of type $[\text{RuCl}(\text{arene})(\text{NHC})\text{L}]^+$,¹⁰ and affords heteroleptic complexes comprising a single (chelating) NHC ligand. Due to the coordination of the carbene ligand, the photophysical and electrochemical properties are significantly altered as compared to the parent $[\text{Ru}(\text{bpy})_3]^{2+}$ system, rendering these complexes potentially useful active sites for photovoltaic applications.

Results and discussion

Synthesis of complexes. Our initial attempts to prepare complexes of type $[\text{Ru}(\text{bpy})_2(\text{C}^{\wedge}\text{N})]^{2+}$ (where $\text{C}^{\wedge}\text{N}$ represents a *C,N*-bidentate carbene-imidazole ligand) focused on using $\text{Ru}(\text{bpy})_2\text{Cl}_2$ as starting material.¹¹ However, substitution of the chlorides by the carbene ligand either via the free carbene route or via transmetallation protocols¹² from the corresponding silver carbene intermediate failed. As a consequence, the reaction sequence for installing the ligands was changed and the carbene was coordinated prior to the pyridine ligands. Complexes **2** were thus obtained via a silver carbene intermediate, generated in situ by adding Ag_2O to the carbene ligand precursor **1**, and subsequent transmetallation with $[\text{RuCl}_2(\text{cymene})]_2$ via standard methods (Scheme 1).¹²

Scheme 1



The formation of complexes **2** was evidenced by spectroscopic and mass spectrometric analyses. The ^1H NMR spectra of both complexes revealed a diagnostic AB doublet for the bridging CH_2 group between 5 and 6 ppm ($^2J_{\text{HH}} = 16.8$ and 16.5 Hz for **2a** and **2b**, respectively). Diastereotopicity of the methylene protons indicated chelation of the carbene ligand. The carbene carbon appeared at δ_{C} 171 and 171.3 (**2a** and **2b**, respectively) in the ^{13}C NMR spectra. An X-ray diffraction analysis of the PF_6^- -salt of **2a** confirmed the structure surmised from analyses in solution (Fig. 2).

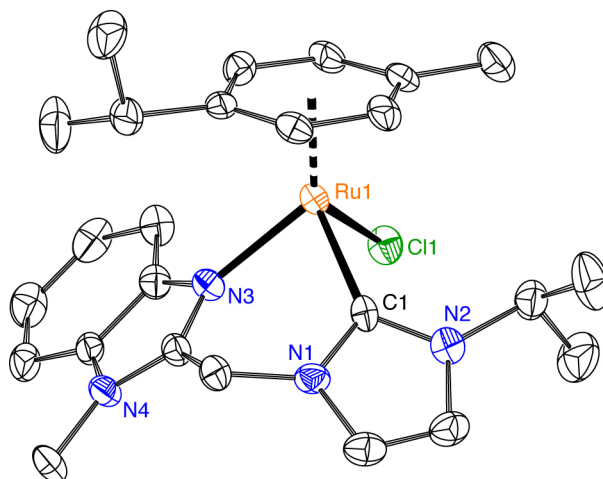


Figure 2. ORTEP representation of complex **2a** (30% probability level); hydrogen atoms and non-coordinated Cl^- anion omitted for clarity. The unit cell contains two crystallographically independent molecules with statistically identical structural parameters. Selected bond lengths and angles: Ru1–C1 2.054(6) Å, Ru1–N3 2.099(4) Å, C1–Ru1–N3 82.6(2)°.

Subsequent displacement of the arene ligand from complexes of type $\text{Ru}(\text{arene})(\text{phenylpyridine})\text{X}$ with bpy was reported to occur in MeCN at room temperature.¹³ While complexes **2** were exceedingly stable under these conditions, smooth substitution of cymene was observed upon heating complex **2a** in DMSO in the presence of bpy and AgPF_6 , indicated by a diagnostic color change of the reaction mixture from bright orange to dark red. Benzene displacement from complex **2b** required slightly less harsh conditions (150 °C, 15 h) than the dissociation of cymene (170 °C, 20 h), however, the latter proceeded cleaner and its arene precursor complex **2** is available in higher yields (71% vs 40%). Therefore the cymene rather than benzene dissociation was the preferred pathway for the synthesis of complex **3** as a $[\text{Ru}(\text{bpy})_3]^{2+}$ analogue comprising a carbene-benzimidazole rather than a third bpy ligand. Formation of

3 was indicated by the absence of the characteristic arene signals in the ^1H NMR spectrum. Instead, 16 mostly well-resolved signals in equal ratios appeared in the aromatic region, supporting the coordination of two bipyridine ligands. In addition, the diastereotopic isopropyl CH_3 groups gave rise to two highfield doublets (δ_{H} 0.35 and 0.91 as compared to δ_{H} 1.3 and 1.6 in **2**), indicating a substantial influence of a pyridine moiety in close proximity. The carbene-imine ligand displayed similar features in **3** as in **2**, *i.e.* an AB doublet (δ_{H} 5.82 and 5.34, $^2J_{\text{HH}} = 17.6$ Hz) for the CH_2 suggesting ligand chelation. The carbene resonance appeared at δ_{C} 180.4 and hence at slightly lower field than in the arene precursors. Unambiguous evidence for the formation of **3** was obtained from a solid state analysis of single crystals grown from slow diffusion of Et_2O into a methanolic solution of **3**. The molecular structure (Fig. 3) features a distorted octahedral ruthenium(II) center that is chelated by the carbene-benzimidazole ligand and by two bpy ligands. The Ru1–C1 bond is slightly shorter than in complex **2** (2.033(3) vs 2.054(6) Å), which is compensated by an elongation of the Ru1–N3 bond (2.119(2) vs 2.099(4) Å). Most interestingly, the Ru1–N8 distance *trans* to the carbene is 2.132(2) Å and hence significantly longer than the remaining Ru–N_{bpy} bonds (average 2.055(15) Å) as a consequence of the stronger *trans* influence of the carbene ligand as compared to the imines. Complex **3** crystallized in the centrosymmetric space group $P2_1/c$, implying the formation of a Δ/Λ -racemic mixture.

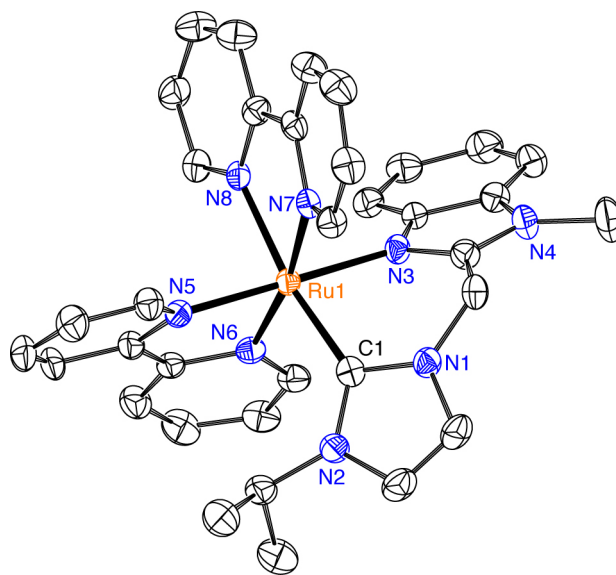
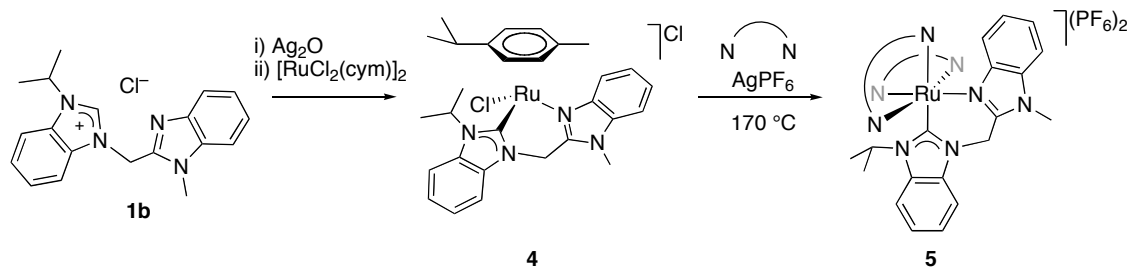


Figure 3. ORTEP representation of complex **3** (50% probability level); hydrogen atoms, co-crystallized MeOH molecule, and non-coordinated PF_6^- anions omitted for clarity. Selected bond lengths (Å): Ru1–C1 2.033(3), Ru1–N3 2.119(2), Ru1–

N5 2.049(2), Ru1–N6 2.044(2), Ru1–N7 2.073(2), Ru1–N8 2.132(2); Selected bond angles (°): C1–Ru1–N3 84.90(10), N5–Ru1–N6 78.97(10), N7–Ru1–N8 77.61(9).

Investigation of the arene displacement reaction revealed that the presence of a silver salt was pivotal. In the absence of AgPF₆, ill-defined product mixtures were obtained along with significant portions of decomposition products. When using MeCN instead of DMSO as solvent under otherwise identical reaction conditions, no bpy coordination was observed and complex **3** did not form in detectable quantities. The reaction proceeded smoothly, however, if the imidazolylidene is replaced by a less basic benzimidazolylidene ligand¹⁴ as in complex **4**, yielding the [Ru(bpy)₃]²⁺ analogue **5** in good yields (Scheme 2). In solution, complex **5** displays features that are strongly related to those of complex **3**, *e.g.*, an AB doublet at δ_H 6.01 and 5.38 (²J_{HH} = 18.0 Hz) for the benzimidazole-benzimidazolylidene methylene bridge. The ¹³C NMR resonance for the ruthenium-bound carbene carbon was located at δ_C 196.2. This downfield shift as compared to the imidazolylidene analogue **3** is in agreement with literature data and has been attributed to a poor overlap of the arene π orbital network with the NCN amidinylidene π orbitals.¹⁵

Scheme 2



Replacing bpy by terpy produced, after stirring for 20 h at 130 °C, complex **7** as a dark purple complex (Scheme 3). At higher temperature, oxidation of the methylene group and concomitant cleavage of the N_{carbene}–C bond takes place as a side reaction and complex **6** featuring a monodentate

carbene and a *N,O*-bidentate chelating benzimidazole-carboxylate ligand was obtained instead along with various undefined products (Fig. 4). Noteworthy, the carbene ligand in complex **6** is an unusual¹⁶ protic NHC ligand, *i.e.* a true tautomer of *N*-alkylated imidazole.

Scheme 3

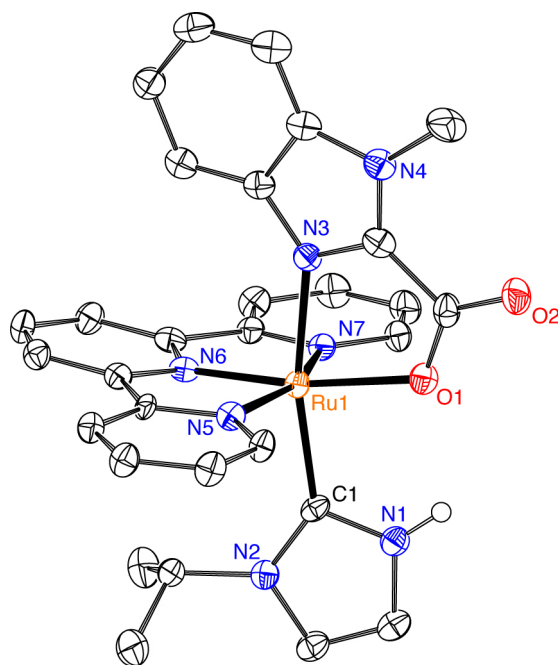
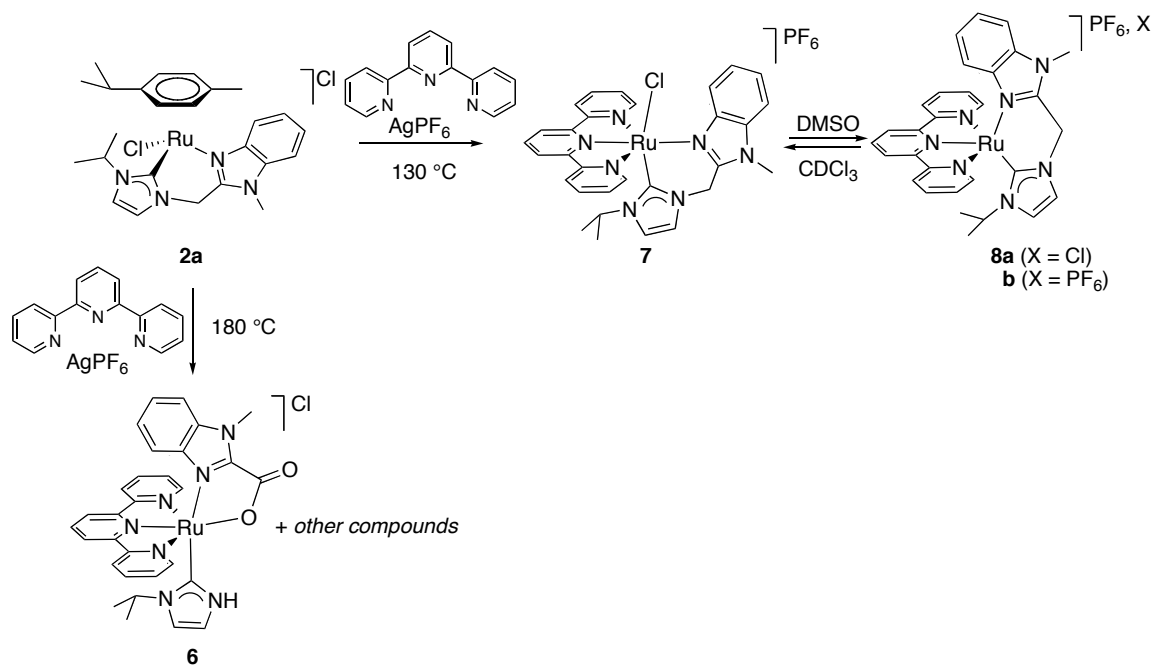


Figure 4. ORTEP representation of complex **6** (50% probability level); all C-bound hydrogen atoms, co-crystallized MeOH molecule, and non-coordinated Cl^- anion omitted for clarity. Selected bond lengths (\AA): $\text{Ru1}-\text{C1}$

2.046(4), Ru1–N3 2.126(3), Ru1–N5 2.077(3), Ru1–N6 1.908(4), Ru1–N7 2.067(3), Ru1–O1 2.141(3); Selected bond angles (°): O1–Ru1–N3 77.13(13), N5–Ru1–N6 80.35(15), N6–Ru1–N7 80.22(15), N3–Ru1–C1 166.88(16), Ru1–C1–N1 120.2(3), Ru1–C1–N2 136.0(3).

Complex **7** has low solubility in CHCl₃ and is essentially insoluble in other apolar solvents. In DMSO-D₆, the terpy signals appeared as six resonances in 2:2:2:2:2:1 integral ratio in the ¹H NMR spectrum, suggesting C_s symmetry of the complex. Likewise, the methylene bridge appeared as a singlet (δ_H 5.80), which is in agreement with a rapid puckering of the bidentate carbene ligand involving wagging about the Ru–C_{carbene} bond. In CDCl₃, some of the terpy resonances were rearranged, which may be rationalized by chloride bonding to ruthenium in apolar solvents (*viz.* **7**) and chloride dissociation and formation of the penta-coordinate complex **8a** in more polar solvents such as DMSO (Scheme 3).¹⁷ In the high-resolution ESI-MS, both the monocation [RuCl(terpy)(carb-benzimi)]⁺ and the dicationic species [Ru(terpy)(carb-benzimi)]²⁺ were detected with the expected isotopic pattern at 624.1219 and 294.5766 *m/z*, respectively. These results suggest a relatively labile coordination of the chloride ligand and support the conclusions from the structural analysis in solution. When complex **7** was treated with an excess AgPF₆, the dicationic complex **8b** was obtained. Complex **8b** was insoluble in CHCl₃, and its ¹H and ¹³C NMR spectroscopic data are identical with those of complex **7** when dissolved in DMSO–D₆. These observations are in line with rapid Cl[–] dissociation from complex **7** in polar solvents.

Spectroscopic and electronic properties. Due to the general interest in the photophysical and electronic properties of [Ru(bpy)₃]²⁺ - and [Ru(terpy)₂]²⁺ -type complexes, complexes **3**, **5**, and **7** were subjected to further analyses. None of the three complexes showed luminescent properties at room temperature. The UV-vis spectra of complexes **3** and **5** featured an MLCT band that is red-shifted as compared to the parent [Ru(bpy)₃]²⁺ complex (Table 1). Slightly lower extinction coefficients were noted. Most interestingly, this lower extinction is accompanied by a considerable broadening of the

MLCT band, thus resulting in a considerably broader absorption window. For example, the extinction coefficient of complex **3** at 570 nm is an appreciable $1500 \text{ M}^{-1} \text{ cm}^{-1}$, while $[\text{Ru}(\text{bpy})_3]^{2+}$ is essentially non-absorbing at this wavelength ($\epsilon_{570} = 200 \text{ M}^{-1} \text{ cm}^{-1}$). Complex **7** is dark purple and shows broad absorption characteristics with λ_{max} at 504 nm.¹⁸ The extinction coefficient drops below $100 \text{ M}^{-1} \text{ cm}^{-1}$ only at wavelengths beyond 760 nm. Such broadening in the visible area may be particularly attractive for better photon harvesting in light-to-energy conversion devices such as solar cells.

Electrochemical analysis of the carbene-modified ruthenium polypyridine complexes **3**, **5**, and **7** were performed using cyclic and differential pulse voltammetry. The bpy-containing complexes **3** and **5** display a fully reversible oxidation at $E_{1/2} = +1.07$ and $+1.16 \text{ V vs SCE}$, respectively ($\Delta E < 80 \text{ mV}$; Table 1). In addition, two reversible reductions were apparent, which were better resolved in complex **5** ($E_{1/2} -1.33$ and -1.56) than in complex **3** (Fig. 5). These features indicate redox properties similar to those of $[\text{Ru}(\text{bpy})_3]^{2+}$, *viz.* bpy-centered reductions and a ruthenium-centered oxidation. Of note, the oxidation potential is significantly lower than that of the parent $[\text{Ru}(\text{bpy})_3]^{2+}$ under identical conditions ($E_{1/2} = +1.39 \text{ V vs SCE}$),¹⁹ indicating that the strong donor properties of the carbene ligand greatly facilitate oxidation processes. Due to the easier oxidation, such systems may be useful for charge separation and hence offer another advantage over $[\text{Ru}(\text{bpy})_3]^{2+}$ -derived dyes in solar cell technology.²⁰ The slightly higher oxidation potential in **5** as compared to complex **3** is in agreement with benzimidazolylidene being a weaker donor ligand than imidazolylidene. The former has been previously compared to saturated imidazolinylidene ligands, reflecting the poor orbital overlap between the benzene fragment and the carbenoid NCN portion of benzimidazolylidenes. These electrochemical measurements suggest that the energy of ruthenium-centered HOMO can be successfully decreased by the introduction of a NHC ligand, while the p-type properties of the complexes are essentially unaltered, preserving the bpy ligands as electron acceptor sites.

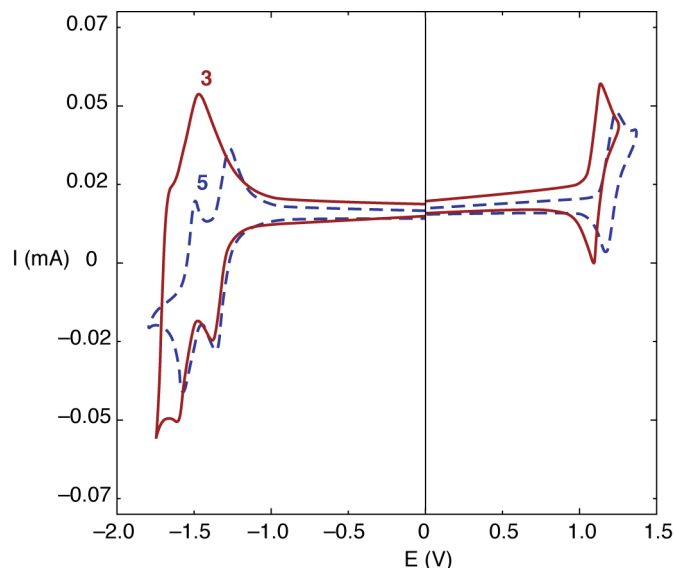


Figure 5. Cyclic voltammograms of complexes **3** (solid line) and **5** (dashed).

Table 1. Spectroscopic and electrochemical data for complexes **3**, **5**, and **7**

complex	$\lambda_{\text{max}} / \text{nm}$ ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$)	$E_{1/2} / \text{mV}$ ($\Delta E / \text{mV}$) ^a
3	481 (11,000)	+1.07 (71), -1.40, ^b -1.55 ^b
5	465 (12,000)	+1.16 (80), -1.33 (84), -1.56 (85)
7	504 (8,900)	+0.73 (44), +1.08 (87), -1.36, ^b -1.53 (89)

^a $\Delta E = E_{\text{pa}} - E_{\text{pc}}$; ^b E_{pc} only

Complex **7** revealed two reversible oxidations at +0.73 and + 1.08 V, which may be rationalized by an equilibrium situation between the octahedral complex **7** and the penta-coordinate dicationic species **8a** in MeCN solution. Tentatively, the lower oxidation may thus be assigned to the monocationic complex **7** and the redox process at +1.08 V to Ru^{II}/Ru^{III} oxidation in complex **8a**.

Conclusions

Novel ruthenium(II) complexes comprising an N-heterocyclic carbene and ancillary polypyridine ligands were successfully prepared from the corresponding Ru(NHC)(arene) precursors via arene displacement. Provided reaction times and conditions are carefully adjusted depending on the starting

material and the polypyridine used, the arene substitution reaction may be of considerable scope as a variety of carbene ruthenium precursors are known and readily accessible. This methodology provides direct access to a diversity of $[\text{Ru}(\text{bpy})_3]^{2+}$ surrogates with modified photochemical and electronic properties, which provide new prospects in DNA intercalation and scission. In addition, such systems may constitute a base for the development of a next generation of active dyes for solar cells, since NHC-modified ruthenium polypyridine complexes display beneficial optical and electrochemical properties. Their application potential in photochemical light-to-energy conversion will be the subject of further investigation in our laboratories.

Experimental Section

General. *N*-isopropyl imidazole, *N*-isopropylbenzimidazole, and 2-chloromethylbenzimidazole were prepared according to literature procedures.²¹ All other reagents were commercially available and used without further purification. NMR spectra were measured at 25 °C on Bruker spectrometers operating at 360, 400, or 500 MHz (¹H NMR spectroscopy) and 100 MHz (¹³C NMR spectroscopy), respectively. Chemical shifts (δ) are referenced to residual solvent signals; coupling constants (J) are reported in Hz. UV-Visible spectra were recorded on a VARIAN Cary 50 spectrometer in CH₃CN. High-resolution ESI-MS measurements were performed in methanol on a Bruker 4.7 BioApex II instrument. Elemental analyses were carried out at the Microanalytical Laboratory of the ETH Zürich (Switzerland).

General procedure for ligand synthesis (A): Ligands were prepared according to adapted literature procedures.^{21d} Thus, *N*-isopropyl (benz)imidazole (2 equiv.) was stirred in CH₃CN (100 mL) at reflux in the presence of 2-chloromethylbenzimidazole (1 equiv.). After 48 h the solution volume was reduced to 10 mL and Et₂O (20 mL) was added to precipitate the product. The formed powder was collected and washed with Et₂O (3 × 10 mL).

General procedure for synthesis of arene containing complexes (B): The ligand precursor (2.1 eq) and Ag₂O (1.6 equiv.) were vigorously stirred in CH₂Cl₂ (10 mL). After 1 h, the mixture was filtered over Celite and washed with CH₂Cl₂ (20 mL). The combined filtrates were added dropwise to a solution of CH₂Cl₂ (10 mL) containing [Ru(arene)Cl₂]₂ (1 equiv.) and stirred for 2 h. The mixture was subsequently filtered over Celite and washed with CH₂Cl₂ (20 mL) then concentrated to about 10 mL. The product precipitated upon addition of Et₂O (100 mL) and was collected and dried. An analytically pure sample was obtained after purification by column chromatography (SiO₂; CH₃CN/H₂O 9:1). Sodium chloride (2 g, large excess) was added to the eluted product solution, then solvents were evaporated and the product was extracted with CH₂Cl₂ and dried.

General procedure for the synthesis of NHC-polypyridine containing complexes (C): The starting ruthenium complex (1 equiv.) and 2,2'-bipyridine (2 equiv.) or 2,2':6,2''-terpyridine (1 equiv.) were stirred in DMSO (5 mL) then AgPF₆ (2.1 equiv.) in DMSO (2 mL) was added dropwise and the reaction mixture was heated. After cooling a precipitate formed, which was eliminated by centrifugation. CH₂Cl₂ (20 ml) was added to the supernatant DMSO solution. After addition of Et₂O (200 mL), a residue formed, which was collected and purified by column chromatography (neutral Al₂O₃; CH₃CN/MeOH 9:1). The red fraction was collected and solvents were evaporated and the product was extracted from the residue with CH₂Cl₂ and dried.

Synthesis of 1a: following procedure A, starting from 1-isopropylimidazol (2.2 g, 20 mmol) and 2-chloromethylbenzimidazole (1.8 g, 10 mmol), **1a** was isolated as a white microcrystalline powder (2.26 g, 78%). ¹H NMR (DMSO-D₆, 500 MHz): δ 9.59 (1H, s, H_{imid}), 8.01, 7.91 (2 × 1H, d, ³J_{HH} 2.2 Hz, CH_{imid}), 7.61, 7.59 (2 × 1H, d, ³J_{HH} 10.0 Hz, CH_{benz}), 7.29, 7.21 (2 × 1H, dd, ³J_{HH} 10.0 Hz, ⁴J_{HH} 0.9 Hz, CH_{benz}), 5.90 (2H, s, CH₂), 4.74 (1H, sept, ³J_{HH} 8.0 Hz, CH_{i-Pr}), 3.89 (3H, s, N-CH₃), 1.51 (6H, d, ³J_{HH} 8.0 Hz, CH_{3 i-Pr}). ¹³C {¹H} NMR (DMSO-D₆, 100 MHz): δ 148.3 (NCN_{benz}), 141.70, 135.9 (2 × C_{benz}), 136.0 (NCHN_{imid}), 123.7 (CH_{imid}), 122.7, 121.9 (2 × CH_{benz}), 120.5 (CH_{imid}), 119.0, 110.4 (2 × CH_{benz}), 52.4

(CH_{i-Pr}), 45.0 (CH₂), 29.2 (N-CH₃ Ar), 22.3 (CH₃ i-Pr). ESI-MS: 255.1606 *m/z*, [C₁₅H₁₉N₄]⁺ requires 255.1609 *m/z*. Calc for C₁₅H₁₉ClN₄ (290.13): C, 61.96; H 6.59; N 19.27. Found: C, 61.88; H, 6.66; N, 19.10.

Synthesis of 1b: Following procedure A, starting from 1-isopropylbenzimidazol (3.2 mg, 20 mmol) and 2-chloromethylbenzimidazole (1.8 g, 10 mmol), **1b** was isolated as a white powder (2.65 g, 78%). ¹H NMR (DMSO-D₆, 400 MHz): δ 10.39 (1H, s, CH_{imid}), 8.17, 8.09 (2 × 1H, d, ³J_{HH} 8.0 Hz, CH_{benzimid}), 7.67 (2H, m, CH_{benzimid}), 7.61, 7.51 (2 × H, d, ³J_{HH} 7.4 Hz, CH_{benz}), 7.26, 7.16 (2 × H, ddd, ³J_{HH} 7.4 Hz, ³J_{HH} 7.4 Hz, ⁴J_{HH} 0.9 Hz, CH_{benz}), 6.24 (2H, s, CH₂), 5.15 (1H, sept, ³J_{HH} 6.8 Hz, CH_{i-Pr}), 3.97 (3H, s, N-CH₃), 1.66 (6H, d, ³J_{HH} 6.8 Hz, CH₃ i-Pr). ¹³C {¹H} NMR (DMSO-D₆, 100 MHz): δ 148.3 (NCN_{benz}), 142.3 (NCHN_{imid}), 142.0, 136.5 (2 × C_{benz}), 132.3, 130.9 (2 × C_{benzimid}), 127.2, 127.0 (2 × CH_{benzimid}), 123.1, 122.3, 119.4 (CH_{benz}), 114.8, 114.5 (2 × CH_{benzimid}), 110.8 (CH_{benz}), 43.8 (CH₂), 51.3 (CH_{i-Pr}), 30.6 (N-CH₃), 22.1 (CH₃ i-Pr). ESI-MS: 305.1770 *m/z*, [C₁₉H₂₁N₄]⁺ requires 305.1776 *m/z*. Calc for C₁₉H₂₁ClN₄ (340.15): C, 66.95; H 6.21; N 16.44. Found: C, 66.98; H, 6.18; N, 16.33.

Synthesis of 2a: According to general procedure B, starting from **1** (203 mg, 0.7 mmol), Ag₂O (123 mg, 0.534 mmol) and [Ru(*p*-cymene)Cl₂]₂ (204 mg, 0.333 mmol), **2a** was obtained as a yellow powder (265 mg, 71%). ¹H NMR (DMSO-D₆, 400 MHz): δ 7.93 - 7.95 (1H, m, CH_{benz}), 7.78 (1H, d, ³J_{HH} 2.0 Hz, CH_{imid}), 7.75 (1H, m, CH_{benz}), 7.69 (1H, d, ³J_{HH} 2.0 Hz, CH_{imid}), 7.41 - 7.47 (2H, m, CH_{benz}), 5.96 (1H, d, ²J_{HH} 16.8 Hz, CH₂), 5.93, 5.87, 5.54, 5.50 (4 × 1H, d, ³J_{HH} 6.0 Hz, CH_{cym}), 5.13 (1H, d, ²J_{HH} 16.8 Hz, CH₂), 4.92 (1H, sept, ³J_{HH} 6.8 Hz, CH_{i-Pr cym}), 3.99 (3H, s, N-CH₃ Ar), 2.59 (1H, sept, ³J_{HH} 6.8 Hz, CH_{i-Pr NHC}), 2.18 (3H, s, CH₃ cym), 1.60, 1.30 (2 × 3H, d, ³J_{HH} 6.8 Hz, CH₃ i-Pr NHC), 1.06, 0.99 (2 × 3H, d, ³J_{HH} 6.8 Hz, CH₃ i-Pr cym). ¹³C {¹H} NMR (DMSO-D₆, 100 MHz): δ 171.9 (C-Ru), 149.1 (NCN), 141.4, 134.4 (2 × C_{benz}), 124.0 (CH_{imid}), 124.0, 123.2 (2 × CH_{benz}), 119.7 (CH_{benz}), 119.2 (CH_{imid}), 111.5 (CH_{benz}), 105.5, 103.8 (2 × C_{cym}), 89.2, 84.9, 84.1, 83.4 (4 × CH_{cym}), 52.1 (CH_{i-Pr cym}), 43.9 (CH₂), 31.0 (N-CH₃ Ar, CH_{i-Pr NHC}), 24.2 (CH₃ i-Pr cym), 24.0, 23.4 (2 × CH₃ i-Pr NHC), 20.3 (CH₃ i-Pr cym), 18.12 (CH₃ cym). ESI-MS: 525.1358 *m/z*, [C₂₅H₃₂ClN₄Ru]⁺ requires 525.1353 *m/z*. Calc for C₂₅H₃₂Cl₂N₄Ru (560.52): C, 53.57; H, 5.75; N,

10.00. Found: C, 53.50; H, 5.72; N, 9.91.

Synthesis of 2b: According to general procedure B, starting from **1** (203 mg, 0.7 mmol) and Ag₂O (0.534 mmol, 123 mg) the filtrates were evaporated and the residual solid was added in portions to a stirred DMF solution of [Ru(benzene)Cl₂]₂ (166 mg, 0.333 mmol in 10 mL) at 70°C. After 18 h the mixture was filtered over Celite and washed with CH₂Cl₂ (20 mL). The product was precipitated by addition of Et₂O (150 mL), collected, and purified by column chromatography (SiO₂; CH₃CN/H₂O 9:1). Sodium chloride (2 g, large excess) was added to the eluted product solution, then solvents were evaporated and the product was extracted with CH₂Cl₂ and dried to afford **2b** as yellow powder (133 mg, 40%). ¹H NMR (DMSO-D₆, 500 MHz): δ 8.15 (1H, d, ³J_{HH} 7.0 Hz, CH_{benz}), 7.76 (1H, d, ³J_{HH} 2.5 Hz, CH_{imid}), 7.74 (2H, m, CH_{benz}, CH_{imid}), 7.44 (2H, m, CH_{benz}), 5.99 (1H, d, ²J_{HH} 16.5 Hz, CH₂), 5.97 (6H, s, CH_{arene}), 5.34 (1H, d, ²J_{HH} 16.5 Hz, CH₂), 5.07 (1H, sept, ³J_{HH} 7.0 Hz, CH_{i-Pr}), 4.00 (2H, s, N-CH₃), 1.60, 1.31 (3H, d, ³J_{HH} 7.0 Hz, CH_{3 i-Pr}). ¹³C {¹H} NMR (DMSO-D₆, 100 MHz): δ 171.3 (C-Ru), 149.6 (NCN), 141.3, 134.4 (2 × C_{benz}), 123.9 (CH_{benz}), 123.9 (CH_{imid}), 123.2, 119.8 (2 × CH_{benz}), 118.9 (CH_{imid}), 111.4 (CH_{benz}), 87.3 (CH_{arene}), 52.1 (CH_{i-Pr}), 44.0 (CH₂), 30.4 (N-CH₃), 23.7, 23.6 (2 × CH_{3 i-Pr}). ESI-MS: 469.0716 *m/z*, [C₂₁H₂₄ClN₄Ru]⁺ requires 469.0727 *m/z*. Calc for C₂₁H₂₄Cl₂N₄Ru (504.04): C, 50.07; H, 4.80; N, 11.11. Found: C, 50.01; H, 4.84; N, 11.08.

Synthesis of 3: According to general procedure C, starting from **2a** (280 mg, 0.5 mmol), AgPF₆ (263 mg, 1.05 mmol) and 2,2'-bipyridine (156 mg, 1.0 mmol), heating to 170 °C for 20 h afforded **3** as orange powder (335 mg, 70%). Simultaneously starting from 253 mg **2b** (253 mg, 0.5 mmol) and heating at 150 °C for 15 h also gave **3** (344 mg, 72%). ¹H NMR (DMSO-D₆, 400 MHz): δ 8.91, 8.80 (2 × 1H, d, ³J_{HH} 8.0 Hz, CH_{bpy}), 8.66 (1H, d, ³J_{HH} 5.2 Hz, CH_{bpy}), 8.61 (1H, d, ³J_{HH} 8.0 Hz, CH_{bpy}), 8.53 (1H, d, ³J_{HH} 8.4 Hz, CH_{bpy}), 8.23 (1H, ddd, ³J_{HH} 8.0 Hz, ³J_{HH} 8.0 Hz, ⁴J_{HH} 1.2 Hz, CH_{bpy}), 8.19 (1H, d, ³J_{HH} 5.2 Hz, CH_{benz}), 8.14 (1H, ddd, ³J_{HH} 8.0 Hz, ³J_{HH} 8.0 Hz, ⁴J_{HH} 1.2 Hz, CH_{bpy}), 7.99-8.03 (3H, m, CH_{benz}, 2 × CH_{bpy}), 7.64 - 7.69 (2H, m, CH_{imid}, CH_{bpy}), 7.65 (2H, m, CH_{bpy}), 7.59 (1H, d, ³J_{HH} 2.0 Hz, CH_{imid}), 7.51 - 7.45 (2H, m, 2 × CH_{benz}), 7.31 (1H, ddd, ³J_{HH} 8.4 Hz, ³J_{HH} 8.4 Hz, ⁴J_{HH} 0.9 Hz, CH_{bpy}), 7.22, 6.86 (2 ×

1H, dd, $^3J_{\text{HH}}$ 7.6 Hz, $^4J_{\text{HH}}$ 1.0 Hz, CH_{bpy}), 6.05 (1H, d, $^3J_{\text{HH}}$ 8.4 Hz, CH_{bpy}), 5.82, 5.34 (2 × 1H, d, $^2J_{\text{HH}}$ 17.6 Hz, CH₂), 3.92 (3H, s, N-CH₃), 2.99 (1H, septet, $^3J_{\text{HH}}$ 6.8 Hz, CH_{i-Pr}), 0.91, 0.35 (2 × 3H, d, $^3J_{\text{HH}}$ 6.8 Hz, CH_{3 i-Pr}). ¹³C {¹H} NMR (DMSO-D₆, 100 MHz): δ 180.4 (Ru-C), 157.8, 157.4, 157.1, 156.1 (4 × C), 155.2 (CH_{bpy}), 153.4 (CH_{benz}), 151.5 (C), 150.9 (CH_{bpy}), 149.9 (CH_{benz}), 141.3 (C), 138.2, 137.3, 136.9, 136.4 (4 × CH_{bpy}), 135.1 (C), 127.4, 126.6 (2 × CH_{bpy}), 126.6, 126.1 (2 × CH_{benz}), 125.4 (CH_{imid}), 124.6, 124.5, 124.4, 123.6, 123.5, 122.9 (6 × CH_{bpy}), 118.6 (CH_{imid}), 116.2, 111.9 (2 × CH_{bpy}), 49.4 (CH_{i-Pr}), 44.6 (CH₂), 30.9 (N-CH₃), 22.3, 21.9 (2 × CH_{3 i-Pr}). ESI-MS: 334.0976 *m/z*, [C₃₅H₃₄N₈Ru]²⁺ requires 334.0974 *m/z*. Calc for C₃₆H₃₈N₈OF₁₂P₂Ru (958.12) × CH₃OH: C, 43.68; H, 3.87; N, 11.32. Found: C, 43.65; H, 3.85; N, 11.33.

Synthesis of 4: According to general procedure B, starting from **1b** (182 mg, 0.534 mmol), Ag₂O (123 mg, 0.534 mmol) and [Ru(*p*-cymene)Cl₂]₂ (204 mg, 0.333 mmol), **4** was obtained as yellow powder (284 mg, 70%). ¹H NMR (DMSO-D₆, 400 MHz): δ 8.24 (1H, d, $^3J_{\text{HH}}$ 8.3 Hz, CH_{benz}), 7.99 - 8.02 (2H, m, CH_{benz}, CH_{benzimid}), 7.77 (1H, m, CH_{benzimid}), 7.38 - 7.46 (4H, m, CH_{benz}, CH_{benzimid}), 6.25 (1H, d, $^2J_{\text{HH}}$ 16.9 Hz, CH₂), 6.04 (2H, m, CH_{cym}), 5.70 (2 × 1H d, $^3J_{\text{HH}}$ 6.2 Hz, CH_{cym}), 5.48 (1H, sept, $^3J_{\text{HH}}$ 7.0 Hz, CH_{i-Pr cym}), 5.27 (1H, d, $^2J_{\text{HH}}$ 16.9 Hz, CH₂), 4.11 (3H, s, N-CH₃), 2.68 (1H, sept, $^3J_{\text{HH}}$ 6.8 Hz, CH_{i-Pr NHC}), 2.16 (3H, s, CH_{3 cym}), 1.88, 1.56 (2 × 3H, d, $^3J_{\text{HH}}$ 7.0 Hz, CH_{3 i-Pr cym}), 1.06, 1.02 (2 × 3H, d, $^3J_{\text{HH}}$ 6.8 Hz, CH_{3 i-Pr NHC}). ¹³C {¹H} NMR (DMSO-D₆, 100 MHz): δ 172.0 (C-Ru), 149.3 (NCN), 141.4 (C_{benz}), 135.5, 135.0 (2 × C_{benzimid}), 132.1 (C_{benz}), 123.6, 123.6, 123.7, 124.6 (2 × CH_{benz}, 2 × CH_{benzimid}), 120.1 (CH_{benz}), 113.2, 112.2 (2 × CH_{benzimid}), 112.0 (CH_{benz}), 107.7, 103.5 (2 × C_{cym}), 89.9, 87.0, 85.9, 84.8 (4 × CH_{cym}), 53.3 (CH_{i-Pr cym}), 42.0 (CH₂), 31.0 (N-CH₃), 30.7 (CH_{i-Pr NHC}), 24.0, 22.0 (2 × CH_{3 i-Pr cym}), 21.5, 21.3 (2 × CH_{3 i-Pr NHC}), 18.5 (CH_{3 cym}). ESI-MS: 575.1538 *m/z*, [C₂₉H₃₄ClN₄Ru]⁺ requires 575.1515 *m/z*. Calc for C₂₉H₃₄Cl₂N₄Ru (610.12): C, 57.05; H, 5.61; N, 9.18. Found: C, 57.10; H, 5.62; N, 9.21.

Synthesis of 5: According to general procedure C, starting from **4** (305 mg, 0.5 mmol), AgPF₆ (263 mg, 1.05 mmol) and 2,2'-bipyridine (156 mg, 1.0 mmol), heating to 170 °C for 20 h afforded **5** as orange powder (373 mg, 74%). ¹H NMR (DMSO-D₆, 400 MHz): δ 9.00 (1H, d, $^3J_{\text{HH}}$ 8.4 Hz, CH_{bpy}), 8.90-8.88

(2H, m, 2 × CH_{bpy}), 8.52 (1H, d, ³J_{HH} 7.6 Hz, CH_{benz}), 8.61 (1H, d, ³J_{HH} 8.4 Hz, CH_{bpy}), 8.29 (1H, ddd, ³J_{HH} 8.0 Hz, ³J_{HH} 8.0 Hz, ⁴J_{HH} 1.4 Hz, CH_{bpy}), 8.21-8.13 (3H, m, 2 CH_{bpy}, CH_{benz}), 8.09-8.01 (3H, m, CH_{bpy}, 2 CH_{benz}), 7.86 (1H, d, ³J_{HH} 5.2 Hz, CH_{bpy}), 7.72 (1H, d, ³J_{HH} 8.0 Hz, CH_{benz}), 7.66-7.62 (2H, m, 2 CH_{bpy}), 7.52, 7.46 (2 × 1H, ddd, ³J_{HH} 7.4 Hz, ³J_{HH} 7.4 Hz, ⁴J_{HH} 1.2 Hz, CH_{benz}), 7.42 (1H, ddd, ³J_{HH} 7.4 Hz, ³J_{HH} 7.4 Hz, ⁴J_{HH} 1.0 Hz, CH_{bpy}), 7.35-7.28 (2H, m, CH_{bpy}, CH_{benz}), 7.22 (1H, dd, ³J_{HH} 7.4 Hz, ⁴J_{HH} 1.1 Hz, CH_{bpy}), 6.87 (1H, ddd, ³J_{HH} 7.4 Hz, ³J_{HH} 7.4 Hz, ⁴J_{HH} 1.0 Hz, CH_{bpy}), 6.60 (1H, d, ²J_{HH} 8.8 Hz, CH_{bpy}), 6.01, 5.32 (2 × 1H, d, ²J_{HH} 18.0 Hz, CH₂), 3.12 (3H, s, N-CH₃), 3.49 (1H, sept, ³J_{HH} 7.2 Hz, CH_{i-Pr}), 1.06, 0.57 (2 × 3H, d, ³J_{HH} 7.2 Hz, CH_{3 i-Pr}). ¹³C {¹H} NMR (DMSO-D₆, 100 MHz): δ 196.2 (Ru-C), 157.7, 157.2, 157.1, 155.8 (4 × C) 155.7, 153.9 (2 × CH_{bpy}), 151.2 (C), 151.0 (CH_{bpy}), 149.9 (CH_{benz}), 140.9 (C), 138.6, 137.7, 138.3 (3 × CH_{benz}), 137.4, 136.8 (2 × CH_{bpy}), 136.6, 135.2, 132.1 (3 × C), 127.6, 126.6, 126.0, 125.0, 124.8, 124.6, 123.6 (7 × CH_{bpy}), 123.4 (CH_{benz}), 122.8 (CH_{bpy}), 122.7, 122.5 (2 × CH_{benz}), 116.3 (CH_{bpy}), 112.1 (CH_{benz}), 111.9, 111.0 (2 × CH_{bpy}), 50.1 (CH_{i-Pr}), 41.7 (CH₂), 31.1 (N-CH₃), 19.6, 18.9 (2 × CH_{3 i-Pr}). ESI-MS: 359.1056 *m/z*, [C₃₉H₃₆N₈Ru]²⁺ requires 359.1053 *m/z*. Calc for C₃₉H₃₆F₁₂N₈P₂Ru (1008.14): C, 46.48; H, 3.60; N, 11.12. Found: C, 46.45; H, 3.61; N, 11.10.

Synthesis of 7: According to general procedure C, starting from **2a** (280 mg, 0.5 mmol), AgPF₆ (263 mg, 1.05 mmol) and 2,2':6,2''-terpyridine (117 mg, 0.5 mmol), heating at 130 °C for 20 h afforded **7** as dark violet powder (272 mg, 70%). ¹H NMR (CD₂Cl₂, 500 MHz): δ 8.62 (1H, d, ³J_{HH} 8.5 Hz, CH_{benz}), 8.38 (2H, d, ³J_{HH} 5.5 Hz, CH_{terpy}), 8.20-8.17 (4H, m, CH_{benz}, CH_{terpy}), 7.88 (3H, m, CH_{terpy}), 7.66 (1H, d, ³J_{HH} 8.5 Hz, CH_{benz}), 7.50 (2H, ddd, ³J_{HH} 7.2 Hz, ³J_{HH} 7.2 Hz, ⁴J_{HH} 0.9 Hz, CH_{terpy}), 7.33 (1H, ddd, ³J_{HH} 7.2 Hz, ³J_{HH} 7.2 Hz, ⁴J_{HH} 0.8 Hz, CH_{terpy}), 7.29 (1H, ddd, ³J_{HH} 8.5 Hz, ³J_{HH} 8.5 Hz, ⁴J_{HH} 1.0 Hz, CH_{benz}), 7.26 (1H, d, ³J_{HH} 1.8 Hz, CH_{imid}), 6.63 (1H, d, ³J_{HH} 1.8 Hz, CH_{imid}), 5.73 (2H, s, CH₂), 4.21 (3H, s, N-CH₃), 3.05 (1H, sept, ³J_{HH} 6.5 Hz, CH_{i-Pr}), 0.52 (6H, d, ³J_{HH} 6.5 Hz, 2 × CH_{3 i-Pr}). The solubility of **7** in CDCl₃ was too low to record a well-resolved ¹³C NMR spectrum. ESI-MS: 294.5766 *m/z*, [C₃₀H₂₉N₇Ru]²⁺ requires 294.5763 *m/z*. Calc for C₃₀H₂₉ClF₆N₇PRu (769.09) × CH₃OH: C, 46.48; H, 4.15; N, 12.24. Found: C, 46.43; H, 4.16; N, 12.20.

Analytical data of 8a (complex **7** dissolved in DMSO): ^1H NMR (DMSO- D_6 , 400 MHz): δ 8.60, 8.59 ($2 \times 2\text{H}$, d, $^3J_{\text{HH}}$ 7.8 Hz, CH_{terpy}), 8.47 (1H, d, $^3J_{\text{HH}}$ 8.4 Hz, CH_{benz}), 8.39 (2H, br, CH_{terpy}), 8.02 – 7.97 (3H, m, CH_{terpy}), 7.84 (1H, d, $^3J_{\text{HH}}$ 8.4 Hz, CH_{benz}), 7.44 – 7.41 (2H, m, CH_{imid} , CH_{benz}), 7.39 (2H, ddd, $^3J_{\text{HH}}$ 7.5 Hz, $^3J_{\text{HH}}$ 7.5 Hz, $^4J_{\text{HH}}$ 1.2 Hz, CH_{terpy}), 7.20 (1H, ddd, $^3J_{\text{HH}}$ 8.4 Hz, $^3J_{\text{HH}}$ 8.2 Hz, $^4J_{\text{HH}}$ 0.9 Hz, CH_{benz}), 7.10 (1H, d, $^3J_{\text{HH}}$ 1.8 Hz, CH_{imid}), 5.80 (2H, s, CH_2), 4.17 (3H, s, N-CH_3), 2.93 (1H, sept, $^3J_{\text{HH}}$ 7.2 Hz, $\text{CH}_{\text{i-Pr}}$), 0.45 (6H, d, $^3J_{\text{HH}}$ 7.2 Hz, $2 \times \text{CH}_3_{\text{i-Pr}}$). ^{13}C $\{^1\text{H}\}$ NMR (DMSO- D_6 , 100 MHz): δ 175.4 (Ru-C), 160.0 ($2 \times \text{C}_{\text{terpy}}$), 159.90 ($2 \times \text{C}_{\text{terpy}}$), 154.2 ($2 \times \text{CH}_{\text{terpy}}$), 150.7 (NCN), 142.5 (C_{benz}), 136.7 ($2 \times \text{CH}_{\text{terpy}}$), 136.1 (C_{benz}), 132.2, (CH_{terpy}), 126.9 ($2 \times \text{CH}_{\text{terpy}}$), 125.0 (CH_{imid}), 124.2 (CH_{benz}), 123.7, 122.4 ($2 \times \text{CH}_{\text{terpy}}$), 122.3 ($2 \times \text{CH}_{\text{benz}}$), 118.0 (CH_{imid}), 111.5 (CH_{benz}), 49.2 ($\text{CH}_{\text{i-Pr}}$), 44.9 (CH_2), 31.5 ($\text{N-CH}_3_{\text{Ar}}$), 22.4 ($\text{CH}_3_{\text{i-Pr}}$).

Synthesis of 8b: According to general procedure C with excess silver salt, starting from **2a** (140 mg, 0.25 mmol), AgPF_6 (197 mg, 0.78 mmol) and terpy (59 mg, 0.25 mmol). Stirring at 130 °C for 20 h afforded **8b** as dark purple powder (163 mg, 72%). An analytically pure sample was obtained by recrystallization from MeOH/Et₂O. ^1H and ^{13}C NMR data are identical to those of **8a**. Calc for $\text{C}_{30}\text{H}_{29}\text{F}_{12}\text{N}_7\text{P}_2\text{Ru}$ (879.08) \times CH_3OH : C, 40.89; H, 3.65; N, 10.77. Found: C, 40.98; H, 3.72; N, 10.68.

Electrochemistry. Electrochemical measurements were carried out using an EG&G Princeton Applied Research Potentiostat Model 273A at 0.1 Vs^{-1} employing a gastight three-electrode cell under an argon atmosphere. A Pt disk with a 3.80 mm^2 surface area was used as the working electrode and was polished before each measurement. The reference electrode was a Ag/AgCl electrode; the counter electrode was a Pt wire. Bu_4NPF_6 (0.1 M) in dry CH_3CN was used as a base electrolyte with analyte concentrations of approximately 1×10^{-3} M. The ferrocenium/ferrocene redox couple was used as an internal reference ($E_{1/2} = 0.46$ vs SCE).²²

Crystal structure determination of complexes 3, 5, and 6. Intensity data for crystals of **3** and **5**

were collected at 130 K for **3** and at 173 K for **5** on a Stoe Mark II-Imaging Plate Diffractometer System using Mo-K α graphite monochromated radiation ($\lambda = 0.71073 \text{ \AA}$). Nominal crystal to detector distances were 120 mm (**3**) and 130 mm (**5**). Data for **6** were collected using an Oxford Diffraction SuperNova A diffractometer fitted with an Atlas detector using Cu-K α radiation ($\lambda = 1.54184 \text{ \AA}$). A complete dataset was collected, assuming that the Friedel pairs are not equivalent.

The structures were solved by direct methods using the program SHELXS-97.²³ Non-hydrogen atoms were refined anisotropically using weighted full-matrix least-squares on F^2 . The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. A numerical absorption correction was applied for **3** using STOE X-Red & X-Shape. Semi-empirical absorption correction was applied for structure **5** using MULscanABS as implemented in PLATON03.²⁴ An analytical absorption correction based on the shape of the crystal of **6** was performed.²⁵

The unit cell of crystals of **3** contains two crystallographically independent complex molecules. The independent PF₆⁻ counterions were disordered (occupancies 0.52/0.48 and 0.81/0.19, respectively). The disorder was resolved by applying restraints to the minor positions using the SAME instruction in SHELXL. The major positions were refined anisotropically, while the minor positions were refined isotropically. In complex **5**, one of the two PF₆⁻ anions was disordered over two positions (occupancies 0.5/0.5). In the final cycles of refinement their anisotropic displacement parameters were made mutually equal using the EADP instruction in SHELXL. Further crystallographic details are compiled in the Supporting Information. CCDC 794590 (**3**), 794591 (**5**), and 794592 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments. We thank O. Schuster (Univ. Fribourg), and A. Neels (CSEM Neuchatel) for crystallographic analyses and C. Gandolfi for electrochemical measurements. This work was supported by the European Research Council and a UCD start-up grant.

Supporting Information Available: Crystallographic data for complexes **3**, **5**, and **6** in CIF format.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

(1) For representative examples, see: (a) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. (b) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85. (c) Purugganan, M. D.; Kumar, C. V.; Turro, N. J.; Barton, J. K. *Science* **1988**, *241*, 1645. (d) Balzani, V.; Juris, A. *Coord. Chem. Rev.* **2001**, *211*, 97. (e) Richter, M. M. *Chem. Rev.* **2004**, *104*, 3003. (f) Constable, E. C. *Chem. Soc. Rev.* **2007**, *36*, 246. (g) Ward, M. D. *Chem. Commun.* **2009**, 4487. (h) Zeglis, B. M.; Boland, J. A.; Barton, J. K. *Biochemistry* **2009**, *48*, 839. (i) Youngblood, W. J.; Lee, S.-H. A.; Maeda, K.; Mallouk, T. E. *Acc. Chem. Res.* **2009**, *42*, 1966.

(2) (a) Desilvestro, J.; Grätzel, M.; Kavan, L.; Moser, J. E.; Augustynski, J. *J. Am. Chem. Soc.* **1985**, *107*, 2988. (b) Hagfeldt, A.; Grätzel, M. *Acc. Chem. Res.* **2000**, *33*, 269. (c) Grätzel, M. *Inorg. Chem.* **2005**, *44*, 6841.

(3) (a) Nazeeruddin, M. K.; Pechy, P.; Renouard, T.; Zakeeruddin, S. M.; Humphry-Baker, R.; Compte, P.; Liska, P.; Cevey, L.; Costa, E.; Shklover, V.; Spiccia, L.; Deacon, G. B.; Bignozzi, C. A.; Grätzel, M. *J. Am. Chem. Soc.* **2001**, *123*, 1613. (b) Chen, C.-Y.; Wu, S.-J.; Wu, C.-G.; Chen, J.-G.; Ho, K.-C. *Angew. Chem., Int. Ed.* **2006**, *45*, 5822. Gao, F.; Wang, Y.; Shi, D.; Zhang, J.; Wang, M.; Jing, X.; Humphry-Baker, R.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2008**, *130*, 10720. (c) Wadman, S. H.; Lutz, M.; Tooke, D. M.; Spek, A. L.; Hartl, F.; Havenith, R. W. A.; van Klink, G. P. M.; van Koten, G. *Inorg. Chem.* **2009**, *48*, 1887. (d) Bessho, T.; Yoneda, E.; Yum, J.-H.; Guglielmi, M.; Tavernelli, I.; Imai, H.; Röthlisberger, U.; Nazeeruddin, M. K.; Grätzel, M. *J. Am. Chem. Soc.* **2009**, *131*, 5930. (e) Grätzel, M. *Acc. Chem. Res.* **2009**, *42*, 1788. For selected recent

examples, see: (f) Smalley, S. J.; Waterland, M. R.; Telfer, S. G. *Inorg. Chem.* **2009**, *48*, 13.

(4) (a) Koizumi, T.; Tomon, T.; Tanaka, K. *Organometallics* **2003**, *22*, 970. (b) Koizumi, T.; Tomon, T.; Tanaka, K. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1969. (c) Koizumi, T.; Tomon, T.; Tanaka, K. *J. Organomet. Chem.* **2005**, *690*, 4272.

(5) Son, S. U.; Park, K. H.; Lee, Y.-S.; Kim, B. Y.; Choi, C. H.; Lah, M. S.; Jang, Y. H.; Jang D.-J. K.; Chung, Y. *Inorg. Chem.* **2004**, *43*, 6896.

(6) Kaufhold, O.; Hahn, F. E.; Pape, T.; Hepp, A. *J. Organomet. Chem.* **2008**, *693*, 3435.

(7) (a) Bourrissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (b) Hahn, F. E.; Jahnke, M. C. *Angew. Chem. Int. Ed.* **2008**, *47*, 3122. (c) Diez-Gonzalez, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612. (d) Poyatos, M.; Mata, J. A.; Peris, E. *Chem. Rev.* **2009**, *109*, 3677. (e) Jacobsen, H.; Correa, A.; Poater, A.; Costabile, C.; Cavallo, L. *Cood. Chem. Rev.* **2009**, *253*, 687.

(8) for examples, see: (a) Boydston A. J.; Bielawski, C. W. *Dalton Trans.* **2006**, 4073. (b) Mercs, L.; Labat, G.; Neels, A.; Ehlers, A.; Albrecht, M. *Organometallics* **2006**, *25*, 5648. (c) Leuthäusser, S.; Schwarz, D.; Plenio, H. *Chem. Eur. J.* **2007**, *13*, 7195. (d) Mercs, L.; Neels, A.; Stoeckli-Evans, H.; Albrecht, M. *Dalton Trans.* **2009**, 71680. (e) Powell, A. B.; Bielawski C. W.; Cowley, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 18232.

(9) Mercs, L.; Albrecht, M. *Chem. Soc. Rev.* **2010**, *39*, 1903.

(10) For representative examples, see: (a) Arnold, P. L.; Scarisbrick, A. C. *Organometallics* **2004**, *23*, 2519. (b) Poyatos, M.; Maise-François, A.; Bellemin-Laponnaz, S.; Peris, E.; Gade, L. H. *J. Organomet. Chem.* **2006**, *691*, 2713. (c) Cariou, R.; Fischmeister, C.; Toupet, L.; Dixneuf, P. H. *Organometallics* **2006**, *25*, 2126. (d) Gandolfi, C.; Heckenroth, M.; Neels, A.; Laurency, G.; Albrecht, M. *Organometallics* **2009**, *28*, 5112. (e) Prades, A.; Viciano, M.; Sanau, M.; Peris, E. *Organometallics* **2008**, *27*, 4254. (f) Mathew, P.; Neels, A.; Albrecht, M. *J. Am. Chem. Soc.* **2008**, *130*, 13534. (g) Ruiz,

J.; Vicente, C.; de Haro, C.; Bautista, D. *Dalton Trans.* **2009**, 5071. (h) Zhang, C.; Zhao, Y.; Li, B.; Song, H.; Xu, S.; Wang, B. *Dalton Trans.* **2009**, 5182. (i) Ozdemir, I.; Demir, S.; Gurbuz, N.; Cetinkaya B.; Toupet L.; Bruneau C.; Dixneuf P. H. *Eur. J. Inorg. Chem.* **2009**, 1942. (j) Prades, A; Poyatos, M; Peris, E. *Adv. Synth. Catal.* **2010**, 352, 1155.

(11) (a) Sprintschnik, G.; Sprintschnik, G.; Kirsch, P. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1977**, 99, 4947. (b) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, 17, 3334. (c) Belser, P.; von Zelewsky, A. *Helv. Chim. Acta* **1980**, 63, 1675. (d) Belser, P.; von Zelewsky, A.; Frank, M.; Seel, C.; Vögtle, F.; De Cola, L.; Barigelletti, F.; Balzani, V. *J. Am. Chem. Soc.* **1993**, 115, 4076. For recent examples, see (e) Sun, Y.; Turro, C. *Inorg. Chem.* **2010**, 49, 5025. (f) Ardo, S.; Sun, Y.; Staniszewski, A.; Castellano, F. N.; Meyer, G. J. *J. Am. Chem. Soc.* **2010**, 132, 6696.

(12) (a) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, 17, 972. (b) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, 22, 1663. (c) Garrison, J. C.; Youngs, W. J. **2005**, 105, 3978.

(13) (a) Le Lagadec, R.; Rubio, L.; Alexandrova, L.; Toscano, R. A.; Ivanova, E. V.; Meskys, R.; Laurinavicius, V.; Pfeffer, M.; Ryabov, A. D. *J. Organomet. Chem.* **2004**, 689, 4820. See also: Kuang, D.; Ito, S.; Wenger, B.; Klein, C.; Moser, J.-E.; Humphry-Baker, R.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2006**, 128, 4146.

(14) (a) Amyes, T. L.; Diver, S. T.; Richard, J. P.; Rivas, F. M.; Toth, K. *J. Am. Chem. Soc.* **2004**, 126, 4366. (b) Hahn, F. E.; Le Van, D.; Paas, M.; Fröhlich, R. *Dalton Trans.* **2006**, 860. (c) Gusev, D. G. *Organometallics* **2009**, 28, 6458.

(15) (a) Hahn, F. E.; Wittenbecher, L.; Boese, R.; Bläser, D. *Chem. Eur. J.* **1999**, 5, 1931. (b) Liu, Y.; Lindner, P. E.; Lemal, D. M. *J. Am. Chem. Soc.* **1999**, 121, 10626. (c) Hahn, F. E.; Wittenbecher, L.; Le Van, D.; Fröhlich, R. *Angew. Chem. Int. Ed.* **2000**, 39, 541. (d) Hahn, F. E.; Paas, M.; Le Van, D.;

Lügger, T. *Angew. Chem. Int. Ed.* **2003**, *42*, 5243. (e) Mercks, L.; Neels, A.; Albrecht, M. *Dalton Trans.* **2008**, 5570. (f) Tennyson, A. G.; Rosen, E. L.; Collins, M. S.; Lynch, V. M.; Bielawski, C. W. *Inorg. Chem.* **2009**, *48*, 6924. (g) Er, J. A. V.; Tennyson, A. G.; Kamplain, J. W.; Lynch, V. M.; Bielawski, C. W. *Eur. J. Inorg. Chem.* **2009**, 1729.

(16) for selected examples of other protic carbene complexes, see: (a) Sundberg, R. J.; Bryan, R. F.; Tayloer, I. F.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 381. (b) Clarke, M. J.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 1397. (c) Hahn, F. E.; Tamm, M. *J. Chem. Soc., Chem. Commun.* **1993**, 842. (d) Liu, C.-Y.; Chen, D.-Y.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **1996**, *15*, 1055. (e) Ku, R.-Z.; Chen, D.-Y.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2631. (f) Hahn, F. E.; Langenhahn, V.; Meier, N.; Lügger, T.; Fehlhammer, W. P. *Chem. Eur. J.* **2003**, *9*, 704. (g) Hahn, F. E.; Garcia Plumed, C.; Münder, M.; Lügger, T. *Chem. Eur. J.* **2004**, *10*, 6285. (h) Burling, S.; Mahon, M. F.; Powell, R. E.; Whittlesey, M. K.; Williams, J. M. J. *J. Am. Chem. Soc.* **2006**, *128*, 13702. (i) Ruiz, J.; Perandones, B. F.; Garcia, G.; Mosquera, M. E. G. *Organometallics* **2007**, *26*, 5687. (j) Holanda, A. K. M.; da Silva, F. O. N.; Sousa, J. R.; Diogenes, I. C. N.; Carvalho, I. M. M.; Moreira, I. S.; Clarke, M. J.; Lopes, L. G. F. *Inorg. Chim. Acta* **2008**, *361*, 2929. (k) Kaufhold, O.; Flores-Figueroa, A.; Pape, T.; Hahn, F. E. *Organometallics* **2009**, *28*, 896. (l) Huertos, M. A.; Perez, J.; Riera, L.; Diaz, J.; Lopez, R. *Angew. Chem., Int. Ed.* **2010**, *49*, 6409. (m) Hahn, F. E.; Naziruddin, A. R.; Hepp, A.; Pape, T. *Organometallics* **2010**, *29*, 5283. (n) Dobereiner, G. E.; Chamberlin, C. A.; Schley, N. D.; Crabtree, R. H. *Organometallics* **2010**, *29*, 5728. For a computational study, see (o) Häller, L. J. L.; Macgregor, S. A. *Eur. J. Inorg. Chem.* **2009**, 2000.

(17) Due to the lack of crystallographic evidence, the structure of complex **7** was tentatively surmised to have a mutual *trans* disposition of the chloride and the carbene because of the relative *trans* influences of imines, carbenes, and chlorides.

(18) This absorption band was assigned to the penta-coordinate complex **8a**, while a shoulder around

535 nm may be due to **7**. Notably, this shoulder is missing when complex **8b** was measured in CH₂Cl₂ solution. In MeCN, complexes **8a** and **8b** display essentially identical absorption properties (λ_{max} 503 nm, shoulder around 530 nm). The shoulder may tentatively be attributed to the solvento analogue of **7**, corroborating the identical ¹H NMR spectra of **7** and **8b** in MeCN-D₃.

(19) Mabrouk, P. A.; Wrighton, M. S. *Inorg. Chem.* **1986**, *25*, 526.

(20) Bredas, J.-L.; Norton, J. E.; Cornil, J.; Coropceanu, V. *Acc. Chem. Res.* **2009**, *42*, 1691.

(21) (a) Wilson, J. G.; Hunt F. C.; *Aust. J. Chem.* **1983**, *36*, 2317. (b) Albrecht, M.; Miecznikowski, J. R.; Samuel, A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 3596. (c) Starikova, O. V.; Dolgushin, G. V.; Larina, L. I.; Ushakov, P. E.; Komarova, T. N.; Lopyrev, V. A. *Russ. J. Org. Chem.* **2003**, *39*, 1467. (d) Li, F.; Bai, S.; Hor, T.S. A. *Organometallics* **2008**, *27*, 672.

(22) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

(23) Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.

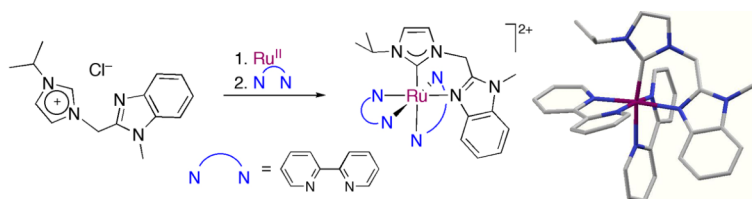
(24) Spek, A. L. *Acta Cryst.* **2009**, *D65*, 148.

(25) Program CrysAlisPro Version 1.171.33.55, Oxford Diffraction Limited, 2010.

for table of contents use only

[Ru(bpy)₃]²⁺ analogues containing a N-heterocyclic carbene ligand

Wadih Ghattas, Helge Müller-Bunz, and Martin Albrecht*



Coordination of a chelating carbene to ruthenium followed by substitution of the ancillary ligands by bi- or terpyridine provides access to carbene complexes which are analogous to [Ru(bpy)₃]²⁺ and which feature electrochemical and spectroscopic properties that are attractive for application in domains such as photosensitization.