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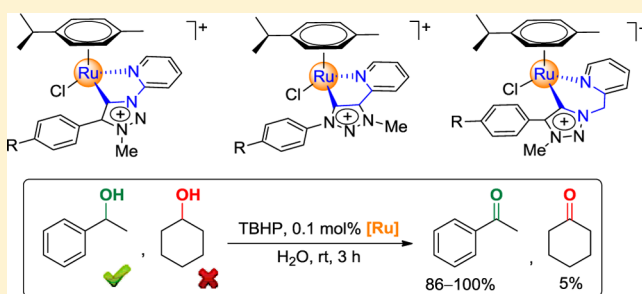
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Supporting Information

ABSTRACT: 1-(2-Pyridyl)-, 4-(2-pyridyl)-, 1-(2-picolyl)-, and 4-(2-picolyl)-functionalized 1,2,3-trisubstituted 1,2,3-triazolium salts (**1A–D**, respectively) were investigated as N-heterocyclic carbene (*trz*NHC) precursors for bidentate coordination to ruthenium(II) through the C^{NHC} and N^{pyridyl} donors. In addition to the pyridyl and picolyl pendant groups, a variety of para-substituted phenyl rings were attached to the 1,2,3-triazolylidene via carbon or nitrogen atoms. The ruthenation was accomplished by metalation with Ag₂O to form intermediate silver carbene complexes and subsequent transmetalation with [Ru(η^6 -*p*-cymene)Cl₂]₂. The cationic ruthenium complexes [Ru(η^6 -*p*-cymene)(*trz*NHC)Cl]⁺ (**3A–C**) were readily obtained with 1-(2-pyridyl)-, 4-(2-pyridyl)-, and 1-(2-picolyl)-1,2,3-triazolium salts (**1A–C**) but not with the 4-picolyl analogue (**1D**). The bidentate coordination of the ligand precursors **1** was followed by multinuclear NMR spectroscopy, revealing significant changes in chemical shifts for triazole C-5, pyridine nitrogen atoms, and the neighboring α -proton (H-6^{pyridyl}) in ¹³C, ¹⁵N, and ¹H NMR spectra. The molecular composition of complexes **3A–C** was confirmed by elemental analysis and positive ion electrospray ionization (ESI⁺) mass spectra, the latter showing ions corresponding to [Ru(η^6 -*p*-cymene)(*trz*NHC)Cl]⁺. The solid-state structures of the three representative complexes were confirmed by single-crystal X-ray analyses; all complexes displayed a typical piano-stool type configuration. Preliminary catalytic activity screening of **3A–C** in the oxidation of selected primary and secondary alcohols with *tert*-butyl hydroperoxide (TBHP) to give carbonyl compounds is also discussed.



INTRODUCTION

Owing to the seminal work by Öfele¹ and Wanzlick² in 1968 on the first metal complexes containing an N-heterocyclic carbene (NHC), followed by Arduengo's report on the isolation and stability of free NHCs in 1991,³ the organometallic chemistry of these ligands has witnessed an explosive development.^{4–6} The success can be attributed to the fact that the complexes of these ligands are remarkably robust toward decomposition and extremely active in catalysis.

1,2,3-Triazol-5-ylidenes have recently emerged as a new subclass of abnormal/mesoionic carbenes (*trz*NHCs).^{7–13} These are of particular interest due to their combination of very high donor strength and ease of synthetic access through the initial triazole formed by the copper-catalyzed azide–alkyne cycloaddition reaction (CuAAC) followed by N-methylation. Specific structural and electronic features place the donor abilities of these mesoionic carbene ligands between those of the most donating normal imidazol-2-ylidenes and abnormal imidazol-4-ylidenes.⁷

Coordination compounds with pyridyl-functionalized *trz*NHCs possess remarkable catalytic, spectroscopic, and

electrochemical properties. This is illustrated by ruthenium coordination compound **I** (Figure 1), showing about 100 times higher catalytic activity for water oxidation in comparison to the analogous pyridine- and phthalazine-based ruthenium complexes.^{14,15} Compounds **II**¹⁶ and **III**¹⁷ have been designed for applications in dye-sensitized solar cells, with the latter showing

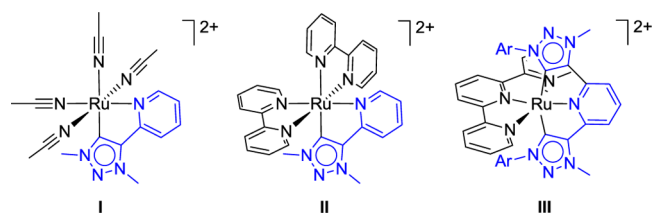


Figure 1. Selected coordination compounds **I–III** with pyridyl-functionalized *trz*NHCs.

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the highest radiative lifetime in comparison to all structurally related complexes.

Aiming at increasing the functionality of the 1,2,3-triazol-5-ylidene ligands, we recently developed a selective approach to the isomeric and homologous pyridyl-functionalized triazolium salts **1A–D** (Figure 2), which should readily offer the possibility of

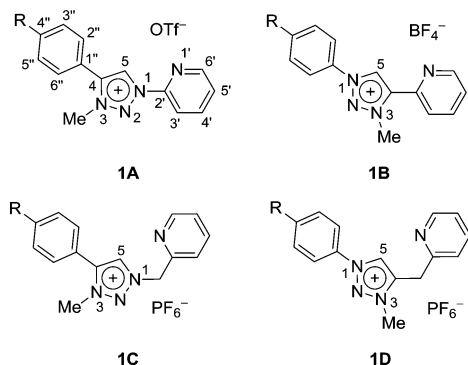


Figure 2. Structures of triazolium salts **1A–D** along with the atom-numbering scheme used for NMR spectral assignment. Numbers without a prime are for the 1,2,3-triazole ring, numbers with a single prime are for the pyridine ring, and numbers with two primes are for the phenyl ring, with C-1'' attached to the triazole.

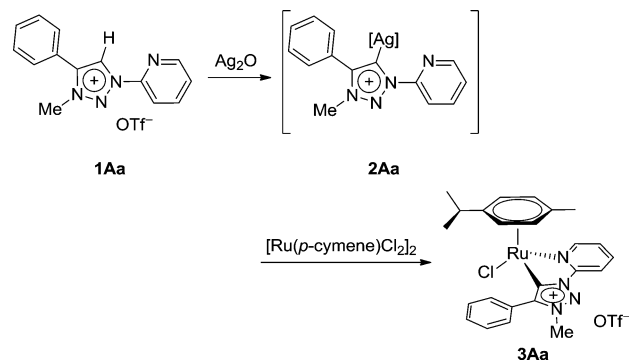
C,N-bidentate coordination by binding to the metal through both the triazole carbenic carbon and pyridyl nitrogen atoms.¹⁸ The synthesis of compounds **1** took advantage of the CuAAC ligation of the appropriate pyridine-bearing “click” partners, i.e., organic azides and terminal alkynes, into the appropriate pyridine-functionalized 1,2,3-triazoles. In a subsequent step these were selectively monomethylated at the triazole N3 atom. The selectivity was achieved through pyridine nitrogen atom protection by N-oxidation.¹⁸

In coordination chemistry, for the ligand precursors **1A–D** it was anticipated that the pyridyl pendant group would modulate the electronic properties of the *trz*NHC ligand as well as provide an opportunity for metal chelation. As chelators, these compounds should easily offer the formation of five- and six-membered metallacycles, with or without the π overlap between the pyridine and *trz*NHC rings, with specific ligand geometry, including bite angle and fine-tuned electronic properties. Here we report their use as C,N-bidentate ligands in (η^6 -*p*-cymene)-ruthenium(II) complexes, along with some preliminary catalytic activity screening.

RESULTS AND DISCUSSION

Synthesis and NMR Spectroscopy Data. The library member **1Aa** was selected as a model substrate for ruthenation, which was obtained by employing the established transmetalation procedures shown in Scheme 1.^{5,7,9,10} When **1Aa** was reacted with Ag₂O in dry acetonitrile at room temperature to form the silver carbene complex **2Aa**, the latter was subjected without isolation to transmetalation into **3Aa** by the addition of [Ru(η^6 -*p*-cymene)Cl₂]₂. The formation of the silver carbene complex **2Aa** from **1Aa** was deduced by ¹H NMR spectral analysis of the reaction mixture by disappearance of the triazolium H-5 proton, resonating at δ 9.04 ppm, from the spectra. We were not successful in obtaining more experimental data for the structure of **2Aa** by NMR, mass spectrometry, or isolation due to its instability. Despite the fact that some silver

Scheme 1



*trz*NHC complexes have been isolated and characterized, their tendency to decompose is also well documented.^{6,7}

Next, the above reaction conditions were employed for the series of ligand precursors **1Aa–g**, differently substituted at the phenyl ring. Upon reaction with Ag₂O the formation of the silver intermediate complexes **2Aa–g** took 2–5 days (Table 1, Time

Table 1. Synthesis of Complexes **3A**

1A	R	Time 1 (days)	Time 2 (h)	3A , yield (%) ^a
1Aa	H	3	2	3Aa , 86
1Ab	CH ₃	2	2	3Ab , 96
1Ac	OCH ₃	5	2	3Ac , 92
1Ad	CN	2	2	3Ad , 91
1Ae	CF ₃	2	2	3Ae , 89
1Af	Br	2	2	3Af , 97
1Ag	NO ₂	2	2	3Ag , 85

^aPercent overall yield of the pure product.

1). The progress of the reactions was monitored by taking aliquots of the reaction mixtures and subjecting them to instant ¹H NMR analyses in DMSO-*d*₆, monitoring the disappearance of the triazolium H-5 proton, as mentioned above. Upon the addition of [Ru(η^6 -*p*-cymene)Cl₂]₂ the subsequent carbene transfer to the ruthenium was completed in just 2 h, as determined by TLC analysis (Time 2). A simple three-step filtration–solvent evaporation–crystallization workup afforded pure **3Aa–g** in excellent 85–97% overall yields.

Ligand precursors from the series **1Ba–f** were allowed to react by the same pathway outlined in Scheme 1, and the results are summarized in Table 2. Here too the slow formation of the intermediate silver carbene complexes **2B** was followed by rapid ruthenation with [Ru(η^6 -*p*-cymene)Cl₂]₂ to give **3Ba–f** in 72–91% overall yield after isolation.

In contrast to the pyridyl-triazolium cations **1A,B**, the activation of the picolyl-triazolium cations **1C** with Ag₂O turned out to be sluggish and did not proceed to completion by using the above reaction conditions. Initial attempts to accelerate the formation of the intermediate silver complexes **2C** were made by employing equimolar amounts of a base additive such as Cs₂CO₃ and Et₃N. In those cases the conversion of **1C** into **2C** was instant as indicated by ¹H NMR analysis, but the subsequent

Table 2. Synthesis of Complexes 3B

1B	R	Time 1 (days)	Time 2 (h)	3B, yield (%) ^a
1Ba	H	4	2	3Ba, 78
1Bb	CH ₃	3	2	3Bb, 81
1Bc	OCH ₃	6	2	3Bc, 91
1Bd	CN	7	2	3Bd, 80
1Be	CF ₃	6	2	3Be, 72
1Bf	Br	3	2	3Bf, 87

^aPercent overall yield of the pure product.

ruthenation with $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\text{Cl}_2]_2$ into 3C did not proceed. An additional screening finally revealed that, rather than the use of additives, the reaction of 1C with Ag_2O conducted with gentle heating to 60 °C proved beneficial. ^1H NMR analysis showed that the formation of the intermediate silver complexes 2Ca–e,h was complete in 2–10 h. In sharp contrast to the ruthenation of 2A,B, however, the reaction of 2Ca–e,h with $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\text{Cl}_2]_2$ to give the final Ru–trznHC compounds 3Ca–e,h required 2–4 days for completion. The 4-chlorophenyl triazolium cation 2Ch was examined instead of the 4-bromo derivative, in comparison to the 3A,B series. Unlike the 3A,B compound series, pure products 3Ca–e,h could only be obtained after flash chromatographic purification, resulting in a substantial drop in the yields (Table 3).

Table 3. Synthesis of Complexes 3C

1C	R	Time 1 (h)	Time 2 (days)	3C, yield (%) ^a
1Ca	H	4	2	3Ca, 50
1Cb	CH ₃	8	2	3Cb, 45
1Cc	OCH ₃	10	4	3Cc, 40
1Cd	CN	3	2	3Cd, 38
1Ce	CF ₃	2	2	3Ce, 45
1Ch	Cl	9	2	3Ch, 42

^aPercent overall yield of the pure product.

Unexpectedly, the complexation of the compound series 1D (1Da (R = H), 1Dc (R = OCH₃), and 1De (R = CF₃); Figure 2) under the reaction conditions described above, either those for the preparation of 3A,B or those for 3C, failed and only the triazolium ions could be isolated.

The above results revealed a significant difference in the reactivity of the isomeric and homologous triazolium cations 1A–C toward Ag_2O . The silver complexation occurs through a triazolium ring deprotonation by the silver base.⁵ The idea that the acidity¹⁹ difference between the variously substituted triazoles in 1A–C is playing a role was qualitatively supported by hydrogen–deuterium exchange NMR experiments.²⁰ Monitoring the aqueous solution chemistry of 1Aa–1Ca in a mixture

of DMSO-*d*₆ and D₂O (6:1 volume ratio) at 296 K by time-dependent NMR spectroscopy indicated a complete exchange of H-5 at 1Aa (9.04 ppm) and 1Ba (10.18 ppm) within 5 h, whereas under the same reaction conditions 1Ca and 1Da remained intact. The hydrogen–deuterium exchange at the last two triazolium cations only occurred after 13 h of heating to 80 °C and was accompanied by deuterium exchange of the bridging methylene protons. An increased acidity of H-5 in the series of the pyridyl-triazolium cations 1Aa and 1Ba over the picolyl analogues 1Ca and 1Da is expected due to the σ -electron-withdrawing pyridine ring attached directly to the triazolium manifold in the former, increasing the electron deficiency of the cationic ring.

All Ru–trznHC compounds 3 in this investigation were fully characterized by multinuclear 1D and 2D NMR spectroscopy, high-resolution mass spectrometry with electrospray ionization, and elemental analysis. For the *p*-cymene ligand, a doublet for each of the four ring protons and two doublets for the methyl groups of the isopropyl group in the ^1H NMR spectra suggested the asymmetry of the coordinated *p*-cymene ring. This was corroborated by the presence of six nonequivalent aromatic *p*-cymene carbon resonances in ^{13}C NMR spectra. ^1H NMR spectroscopy revealed the absence of the low-field triazolium H-5 proton resonance (for the atom-numbering scheme, see Figure 2).

As expected for the bidentate C,N-coordination, the binding of the triazolium cation 1 to give the ruthenium compounds 3 induced the largest changes in the chemical shifts for the triazole C-5 carbon atom, pyridine nitrogen N-1', and the neighboring α -proton H-6'. The corresponding ^1H , ^{13}C , and ^{15}N NMR chemical shifts data along with the coordination shifts (Δ^{H} _{coord}, $\Delta^{^{13}\text{C}}$ _{coord}, $\Delta^{^{15}\text{N}}$ _{coord}) are collected in Table 4. The latter are defined as the difference between the chemical shift of the triazolylidene ligand in its complex and that of the triazolium cation: i.e., $\Delta_{\text{coord}} = \delta_{\text{complex}} - \delta_{\text{triazolium cation}}$.

For a given R = H, in comparison to the triazolium cation C-5 carbon resonances in the ligand precursors 1Aa–1Ca, the corresponding carbenic C-5 resonances in 3Aa–3Ca shifted upfield for $\Delta^{^{13}\text{C}}$ _{coord} = 45.2, 46.0, and 29.9 ppm, respectively (Table 4). Whereas $\Delta^{^{13}\text{C}}$ _{coord} parameters were similar for 3Aa and 3Ba, significantly smaller changes in the chemical shifts were observed for the coordination of 1Ca. No obvious correlation with the varying electronic nature of the substituents R within each series of compounds A–C could be observed.

The pyridine ring protons H-6' were deshielded with $\Delta^{\text{H-6'}}$ _{coord} parameters of 0.47, 0.42, and 0.92 ppm for 3Ad–3Cd, respectively (Table 4). Here too the coordination shifts for 3Ad and 3Bd were similar yet much smaller in comparison to that for 3Cd.

A deshielding of the neighboring α -proton is a good indication of the pyridine nitrogen coordination to the metal.²¹ Additionally, the coordination of the pyridine group was confirmed through the ^{15}N NMR data. The binding of the pyridine ring to ruthenium resulted in a large upfield ^{15}N coordination shift of $\Delta^{\text{N-1'}}$ _{coord} = 60–77 ppm (Table 4). The values are in good agreement with the data reported in the literature for pyridine–ruthenium(II) coordination.²²

Although the coordination shift parameters for 3A–C could reflect the distinct coordination bond lengths and the complex geometries, these should be taken with caution, because it has been demonstrated that the interpretation of the coordination shift in terms of coordination strength must consider the NMR

Table 4. H-6', C-5, and N-1' Chemical and Coordination Shifts (δ and $\Delta_{\text{coord}} = \delta_{\text{complex}} - \delta_{\text{triazolium cation}}$; ppm) for Ruthenium(II) Complexes 3A–C with Triazolium Salts 1A–C

compd	R	solvent	$\delta^{\text{H-6'}}$	$\Delta^{\text{H-6' coord}}$	$\delta^{\text{C-5}}$	$\Delta^{\text{C-5 coord}}$	$\delta^{\text{N-1'}}$	$\Delta^{\text{N-1' coord}}$
1Aa ^a	H	CDCl ₃	8.60		124.4		288 ^b	
3Aa	H	CDCl ₃	9.35	0.75	169.5	45.2	226	−62
1Ab ^a	CH ₃	CDCl ₃	8.60		124.2		287 ^b	
3Ab	CH ₃	CDCl ₃	9.40	0.80	169.5	45.3	226	−61
1Ac ^a	OCH ₃	CDCl ₃	8.60		123.9		286 ^b	
3Ac	OCH ₃	CDCl ₃	9.36	0.76	169.3	45.4	226	−60
1Ad ^a	CN	DMSO- <i>d</i> ₆	8.81		126.8		287 ^b	
3Ad	CN	CDCl ₃	9.28	0.47	170.1	43.3	225	−62
1Ae ^a	CF ₃	DMSO- <i>d</i> ₆	8.81		126.7		287 ^b	
3Ae	CF ₃	CDCl ₃	9.31	0.50	169.8	43.2	226	−61
1Af ^a	Br	DMSO- <i>d</i> ₆	8.80		126.1		287 ^b	
3Af	Br	CDCl ₃	9.30	0.50	169.5	43.4	226	−61
1Ag ^a	NO ₂	DMSO- <i>d</i> ₆	8.82		126.9		287 ^b	
3Ag	NO ₂	CDCl ₃	9.26	0.44	170.2	47.3	225	−62
1Ba ^a	H	DMSO- <i>d</i> ₆	8.91		128.0		309 ^b	
3Ba	H	CDCl ₃	9.39	0.48	174.0	46.0	243	−66
1Bb ^a	CH ₃	DMSO- <i>d</i> ₆	8.90		127.8		309 ^b	
3Bb	CH ₃	CDCl ₃	9.41	0.51	173.8	46.0	242	−67
1Bc ^a	OCH ₃	DMSO- <i>d</i> ₆	8.90		127.7		309 ^b	
3Bc	OCH ₃	CDCl ₃	9.38	0.48	173.8	46.1	243	−66
1Bd ^a	CN	DMSO- <i>d</i> ₆	8.91		126.1		308 ^b	
3Bd	CN	CDCl ₃	9.33	0.42	174.4	48.3	242	−66
1Be ^a	CF ₃	DMSO- <i>d</i> ₆	8.92		128.5		309 ^b	
3Be	CF ₃	CDCl ₃	9.35	0.43	174.2	45.7	243	−66
1Bf ^a	Br	DMSO- <i>d</i> ₆	8.90		128.2		309 ^b	
3Bf	Br	CDCl ₃	9.34	0.44	174.0	45.8	243	−66
1Ca ^a	H	DMSO- <i>d</i> ₆	8.60		129.7		311 ^b	
3Ca	H	CDCl ₃	9.53	0.93	159.6	29.9	235	−76
1Cb ^a	CH ₃	DMSO- <i>d</i> ₆	8.59		129.4		311 ^b	
3Cb	CH ₃	CDCl ₃	9.51	0.92	159.6	30.2	235	−76
1Cc ^a	OCH ₃	DMSO- <i>d</i> ₆	8.59		129.1		312 ^b	
3Cc	OCH ₃	CDCl ₃	9.52	0.93	159.6	29.5	236	−76
1Cd ^a	CN	DMSO- <i>d</i> ₆	8.60		130.5		312 ^b	
3Cd	CN	CDCl ₃	9.52	0.92	160.3	29.8	235	−77
1Ce ^a	CF ₃	DMSO- <i>d</i> ₆	8.60		130.4		312 ^b	
3Ce	CF ₃	CDCl ₃	9.53	0.93	160.1	29.7	235	−77
1Ch ^a	Cl	DMSO- <i>d</i> ₆	8.60		129.9		312 ^b	
3Ch	Cl	CDCl ₃	9.49	0.89	159.9	30.0	235	−77

^aData collected from ref 18. ^bThis work.

solvent and the nature of the counterion, if present.²³ In our case, the different counterions TfO[−], BF₄[−], and PF₆[−] surround the cationic ruthenium complex in 3A–C. With few exceptions, DMSO-*d*₆ and CDCl₃ were employed for measuring NMR spectra of the ligand precursors 1 and the complexes 3, respectively, as shown in Table 4. The selection of the NMR solvent was based on solubility and stability considerations. Whereas the triazolium salts are sparingly soluble in CDCl₃, complexes 3 slowly decompose upon several hours in DMSO-*d*₆. Nevertheless, NMR results strongly confirm the formation of the bidentate Ru–trznHC complex. Elemental analyses of the complexes suggested their molecular compositions including the counterions OTf[−], BF₄[−], and PF₆[−] in 3A–C, respectively. The presence of these anions was also confirmed by ¹⁹F, ¹¹B, and ³¹P NMR spectroscopy. Positive-ion electrospray ionization (ESI+) mass spectra of complexes 3 showed ions corresponding to [Ru(η^6 -*p*-cymene)(trznHC)Cl]⁺.

The ¹⁵N NMR chemical shifts for the noncoordinated triazole nitrogen atoms N-1, N-2, and N-3 in 3Aa–3Ca were extracted

from the ¹H–¹⁵N HMBC spectra and compared with those for the ligand precursors 1Aa–1Ca (Table S1, Supporting Information). As expected, significantly smaller coordination shifts were observed for those atoms in comparison to those for C-5 and N-1'.

The donor strength of the NHC carbenes has been evaluated on the basis of experimental ¹³C NMR parameters.²⁴ In Pd–trznHC compounds only a moderate influence of the electronic properties of the substituents on δ^{carbene} was observed.^{10,25} In compounds 3 the ¹³C NMR chemical shifts for the C-5 atoms vary significantly between complex series spanning from 159.6 ppm for 3Ca to 169.5 ppm for 3Aa and 174.0 ppm for 3Ba. Electron-withdrawing groups such as CF₃ slightly increase the NMR shifts to 160.1, 169.8, and 174.2 ppm for compounds 3Ce, 3Ae, and 3Be, respectively. On the other hand, for electron-donating groups such as OCH₃ the opposite trend can be seen with $\delta^{\text{C-5}}$ values of 159.6, 169.3, and 173.8 ppm for the complexes 3Cc, 3Ac, and 3Bc, respectively (Table 4). Chemical shifts for complexes 3B are comparable with those for the previously

reported analogues, where also C,N-bidentate triazolyldienes were used (δ^{C-5} ranges from 172.4 to 174.1 ppm).¹⁴ In comparison, the carbene chemical shifts for similar ruthenium-(II) complexes containing monodentate triazolyldienes that involve coordination only through the carbon C-5 vary between 158.5 and 163.0 ppm.^{14,26,27} The difference in the C-5 NMR chemical shifts in the complex series **3Aa**, **3B** versus **3C** might be due to the pyridine moiety directly attached to the triazolyldiene ring in the former, withdrawing some electron density and thus deshielding the carbene resonances. The C-5 chemical shifts in the series **3C**, having a methylene bridge between the pyridine ring and a triazole moiety, are more comparable to those of the carbene monodentate triazolyldiene complexes than to the C,N-bidentate analogues.

Crystallographic Data. Overall we were able to crystallize one complex from each series. Single crystals for both **3Aa** and **3Ca** were obtained by layering a concentrated solution of dichloromethane with hexane at 8 °C. X-ray-quality crystals of **3Bf** were obtained from the NMR tube upon slow evaporation from CDCl₃ at 8 °C. All complexes display a typical piano-stool type structure, as expected for half-sandwich complexes of this type. While **3Bf** crystallizes in the orthorhombic space group *P*₂₁₂₁ as a solvate with one molecule of CDCl₃, the other two molecules were found to crystallize in a triclinic system in the space group *P* $\bar{1}$ with no additional solvent molecules. For additional crystallographic information, see Table S2 (Supporting Information). The distances of Ru1 to the centroids of the *p*-cymene ligands are 1.690(1), 1.701(1), and 1.712(1) Å for **3Aa**, **3Bf**, and **3Ca**, respectively, and are therefore in the range of those for previously reported systems.^{14,28} In all three cases the pyridyl/picolyl-triazolyldiene ligand is bound, as expected, to the ruthenium center via the pyridine nitrogen N4 and the triazolyldiene carbon C5A. All bond lengths and angles are within the expected range: e.g., Ru1–C5A 2.050(4) Å and Ru1–N4 2.133(3) Å for **3Ca** (for more details see Tables 5 and 6). In

Table 5. Selected Bond Lengths (Å) in the Complexes 3Aa, 3Bf, and 3Ca

atoms	3Aa	3Bf	3Ca
Ru1–Cl1	2.394(1)	2.400(1)	2.429(2)
Ru1–C5A	2.033(4)	2.027(2)	2.050(4)
Ru1–N4	2.118(4)	2.124(3)	2.133(3)
C5A–C4A	1.385(6)	1.380(4)	1.412(5)
C4A–N3	1.375(5)	1.366(4)	1.364(5)
N1–N2	1.339(5)	1.350(4)	1.339(4)
N2–N3	1.309(5)	1.314(4)	1.335(4)
N1–C5A	1.373(5)	1.346(4)	1.364(5)
N3–C6A	1.469(5)	1.454(4)	1.461(5)
N1–C1B	1.402(6)	1.426(4)	
C1B–N4	1.338(6)		1.350(5)
C4A–C1	1.472(6)	1.450(4)	1.485(5)
C1–N4		1.353(4)	
N1–C6B			1.468(4)
C6B–C1B			1.516(5)
Ru1–Cym(cent)	1.690(1)	1.701(1)	1.712(1)

all three cases the triazolyldiene ligands show a delocalized electronic structure with a slightly decreased N1–C5A–C4A angle in comparison to the free triazolium cations reported previously (compare Table 6). The chloride ligand Cl1 is terminally bound, and the Ru1–Cl1 bond lengths are all within the expected range.^{9,14,28,29}

Table 6. Selected Bond Angles (deg) in the Complexes 3Aa, 3Bf, and 3Ca

atoms	3Aa	3Bf	3Ca
C5A–Ru1–N4	77.4(2)	76.3(1)	87.8(1)
C5A–Ru1–Cl1	85.5(1)	88.3(1)	85.9(1)
N4–Ru1–Cl1	82.4(1)	85.2(1)	80.8(1)
N1–C5A–C4A	101.8(4)	103.2(3)	101.8(3)

In the case of **3Aa** and **3Bf** the coordinating atoms and the ruthenium form a five-membered planar ring. The dihedral angles of the triazolyldiene ring and the pyridine ring are thereby only 6.7(2) and 3.4(1)° for **3Aa** and **3Bf**, respectively. In contrast to that, in **3Ca** with an additional CH₂ group the coordinating atoms form a six-membered ring in a boat-shaped conformation, similar to that found in the metal complex of an analogous flexible click N,N-chelator with a picolyl-triazole motif (compare structures in Figure 3).^{7,9,30} All distances of the coordinating sites

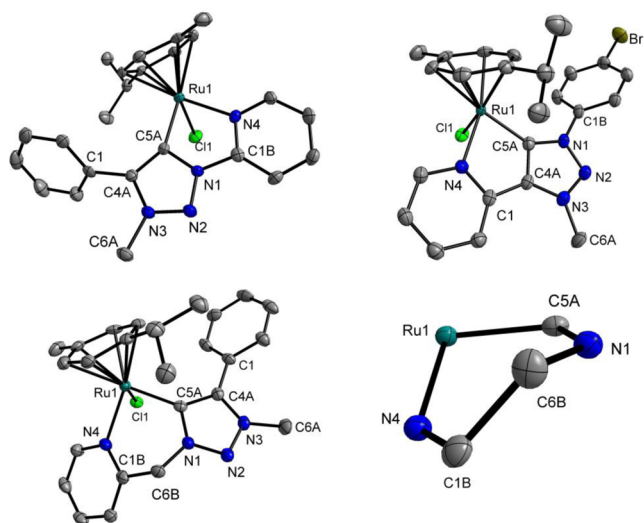


Figure 3. ORTEP plots of the isomers **3Aa** (top left), **3Bf** (top right), and **3Ca** (bottom left) and the boat-shaped configuration of the six-membered ring in **3Ca** (bottom right). The ellipsoids are shown at a probability level of 50%. Hydrogen atoms, solvent molecules, and counterions are omitted for clarity.

to the ruthenium (Ru1–Cl1, Ru1–C5A, Ru1–N4, and Ru1–Cym(cent)) in **3Ca** are slightly elongated in comparison to those in **3Aa** and **3Bf** (Table 5). The additional sp³ carbon atom also results in a large dihedral angle between the picolyl group and the triazolyldiene plane of 45.4(1)°. The (substituted) phenyl residues are strongly shifted toward the triazolyldiene plane by 65.0(2), 47.1(1), and 39.8(1)° for **3Aa**, **3Bf**, and **3Ca**, respectively. For all three structures the packing seemed to be uneventful with no significant short contacts and stacking effects being observed.

Catalytic Activity. With the compounds **3** in hand, we carried out a preliminary investigation of their catalytic activity in the oxidation of selected alcohols with *tert*-butyl hydroperoxide (*t*-BuOOH, TBHP) in water as a solvent. Examples of arene–ruthenium^{31,32} and imidazolium-based Ru–NHC complexes³³ that work efficiently in these systems are well documented, whereas triazolyldiene–ruthenium complexes were recently reported for the oxidation of alcohols.^{26,27} A good to excellent conversion of the two tested secondary benzyl alcohols,³⁴ 1-phenylethanol (**4a**) and 1-phenylpropanol (**4b**), into the

corresponding ketones, acetophenone (**5a**) and propiophenone (**5b**), respectively, was observed by using the different Ru-*trz*NHC complexes **3** (0.1 mol %) in water at room temperature for 3 h (Table 7, entries 1–8). The fact that under the same

Table 7. Oxidation of Selected Secondary Alcohols using Ru-*trz*NHC Complexes **3^a**

entry	alcohol	R ¹	R ²	3	product	conversion (%) ^b
1	4a	C ₆ H ₅	CH ₃	3Aa	5a	100
2	4a	C ₆ H ₅	CH ₃	3Ca	5a	86
3	4a	C ₆ H ₅	CH ₃	3Cc	5a	100
4	4b	C ₆ H ₅	CH ₂ CH ₃	3Aa	5b	90
5	4b	C ₆ H ₅	CH ₂ CH ₃	3Ba	5b	88
6	4b	C ₆ H ₅	CH ₂ CH ₃	3Ca	5b	94
7	4b	C ₆ H ₅	CH ₂ CH ₃	3Cc	5b	94
8	4b	C ₆ H ₅	CH ₂ CH ₃	3Ce	5b	93
9	4c	-(CH ₂) ₅ -		3Ca	5c	5

^aGeneral reaction conditions: a mixture of the alcohol **4a–c** (0.5 mmol), TBHP (2.0 mmol), and Ru catalyst (0.0005 mmol, 0.1 mol %) in distilled water (5 mL) was stirred at room temperature for 3 h. The progress of the reaction was monitored by analyzing aliquots (see the Experimental Section) by ¹H NMR spectroscopy, indicating the presence of the product **5** and in some cases unreacted starting alcohol **4**. ^bDetermined by ¹H NMR spectroscopy.

reaction conditions only minute amounts of cyclohexanone (**5c**) formed from cyclohexanol (**4c**) indicates the selectivity this catalytic system could potentially offer (Table 7, entry 9). Mild reaction conditions requiring the environmentally benign solvent water as well as the above indicated selectivity make our catalytic system superior to some previously known imidazol-2-ylidene-based complexes.³⁵

A potential catalyst recycling was probed with complex **3Aa** (0.0005 mmol, 0.1 mol %), TBHP (2.0 mmol, 4 equiv), and 1-phenylethanol (**4a**, 0.5 mmol) as substrate. After the reaction mixture was stirred for 3 h at room temperature (Table 7, entry 1), the product was isolated by extraction into diethyl ether. For subsequent cycles new portions of 1-phenylethanol (0.5 mmol) and TBHP (2.0 mmol) were added to the water layer and the reaction continued as described above. The conversions were assayed by ¹H NMR analyses of the organic layers to reach 100%, 72%, 51%, 33%, and 28% after each consecutive cycle. Although the loss of structural integrity of the catalysts can be attributed to the drop in the 1-phenylethanol (**4a**) to acetophenone (**5a**) conversion, a steady decrease in its concentration in the reaction mixture caused by the extractive workup over the cycles cannot be ruled out at this point.

Surprisingly, under the same reaction conditions, a primary benzyl alcohol (**4d**) was oxidized into a mixture of benzoic acid (**6a**) and *tert*-butyl esters of peroxybenzoic acids (**7a**) (Table 8, entries 1–5). No other products could be detected in the crude reaction mixtures. Analogous results afforded phenyl-substituted benzyl alcohols (**4e–g**, entries 6–8). To our knowledge, no such transformation to *tert*-butyl peresters has been reported in the literature. Recently, Wan et al. communicated a new synthesis of these compounds from aldehydes and TBHP via Bu₄NI-catalyzed aldehyde C–H oxidation.³⁶

In Table 8 it is intriguing that there are different ratios between the products **6** and **7**, with those in entries 3 and 6 being higher

Table 8. Oxidation of Selected Benzyl Alcohols using Ru-*trz*NHC Complexes **3^a**

entry	alcohol	R	catalyst	time (h)	products 6 , 7 (ratio) ^{b,c}
1	4d	H	3Aa	3	6a , 7a (1.5:1) ^d
2	4d	H	3Ba	3	6a , 7a (1.6:1)
3	4d	H	3Ca	3	6a , 7a (6.0:1)
4	4d	H	3Cc	3	6a , 7a (1.7:1)
5	4d	H	3Ce	3	6a , 7a (1.2:1)
6	4e	2-MeO, 5-Br	3Ca	24	6b , 7b (5.4:1)
7	4f	4-Cl	3Ca	24	6c , 7c (1.5:1)
8	4g	4-MeO	3Ca	24	6d , 7d (2.3:1)

^aGeneral reaction conditions: a mixture of the alcohol **4d–g** (1.0 mmol), TBHP (4.0 mmol), and Ru catalyst (0.001 mmol, 0.1 mol %) in distilled water (5 mL) was stirred at room temperature for the time indicated, and aliquots (see the Experimental Section) were analyzed by ¹H NMR spectroscopy. ^bAs determined by ¹H NMR spectroscopy. ^cA full conversion of the alcohol **4** into a mixture of benzoic acid, **6**, and *tert*-butyl esters of peroxybenzoic acids **7** was noted. ^dProducts were isolated from the reaction mixture by extraction into dichloromethane and separated by column chromatography (light petroleum/ethyl acetate 5/1) to give **6a** and **7a** in 53% and 35% yields, respectively, relative to the starting alcohol **4d**.

than the others. It is reasonable to expect that the oxidation of the primary benzyl alcohols **4** initially affords peroxybenzoic acids **7**, which then undergo decomposition to benzoic acids **6** to the extent that is specific for each present ruthenium complex **3**. An independent experiment where an authentic sample of perester **7a** was subjected to the same reaction conditions as described for the alcohol oxidation (Table 8, footnote a) did not support this idea, as unreacted **7a** was completely recovered from the reaction mixture, with benzoic acid **6a** being undetected. In addition, an alternative that under the applied reaction conditions peresters **7** are formed from benzoic acids **6** was also ruled out by an analogous experiment with **6a** in place of **7a**.

CONCLUSIONS

The scope of the pyridine-functionalized 1,2,3-triazolium salts as N-heterocyclic carbene (*trz*NHC) precursors for bidentate coordination to ruthenium(II) through the C^{NHC} and N^{pyridyl} donors was investigated. In two consecutive steps, in the formation of the intermediate silver carbene complex and in the transmetalation with [Ru(η^6 -*p*-cymene)Cl₂]₂ into cationic [Ru(η^6 -*p*-cymene)(*trz*NHC)Cl]⁺ complexes, both 1-(2-pyridyl)- and 4-(2-pyridyl)-substituted triazolium salts reacted similarly. In contrast, the reactivity of 1-(2-picolyl) and 4-(2-picolyl) analogues turned out to be completely different, demonstrating the large impact of the linker between the pyridine and *trz*NHC donors in ruthenium(II) coordination. NMR spectroscopic data indicate significant modulation of the electronic properties of the carbene center, suggesting the potential of the ligand to fine tune the properties of [Ru(η^6 -*p*-cymene)(*trz*NHC)Cl]⁺ complexes. A preliminary catalytic activity screening of these compounds in TBHP oxidation of the selected primary and secondary alcohols into the carbonyl compounds was surveyed. Although in this particular reaction no change in the catalytic activity between the structurally different complexes could be observed, a consid-

erably faster benzylic oxidation in comparison to nonbenzylic alcohol oxidation was demonstrated.

EXPERIMENTAL SECTION

The reagents and solvents were used as obtained from commercial sources (Sigma-Aldrich). Acetonitrile was dried over 3 Å molecular sieves. The compounds **1**¹⁸ and Ag₂O³⁷ were prepared as described in the literature. The compounds **5a**,^{32,26} **5b**,³² **5c**,³² **6a**,³⁸ **6b**,³⁹ **6c,d**,⁴⁰ and **7a,c,d**³⁶ were (after extractive workup from the crude reaction mixtures by using dichloromethane) identified by comparison of their ¹H NMR spectral data to the literature reports. The *tert*-butyl perester structure of **7b** was assigned on the basis of NMR spectral data comparison with **7a,c,d** and HRMS spectra.

NMR spectra were measured with a 300, 400, and 500 MHz spectrometers, using Si(CH₃)₄ as internal standard. The nitrogen chemical shifts were extracted from ¹H–¹⁵N HMBC spectra. Proton and carbon spectra were referenced to TMS as the internal standard. Some ¹³C chemical shifts were determined relative to the ¹³C signal of the solvent: CDCl₃ (77.0 ppm), DMSO-*d*₆ (39.5 ppm). ¹⁹F NMR, ¹¹B NMR, and ³¹P NMR spectra were referenced to CCl₃F, 15% BF₃ etherate in CDCl₃, and 85% phosphoric acid, respectively, as external standards at δ 0. ¹⁵N chemical shifts were extracted from ¹H–¹⁵N HMBC spectra (with 20 Hz digital resolution in the indirect dimension) with respect to external 90% CH₃NO₂ in CDCl₃ and are corrected to external ammonia by addition of 380.5 ppm. Chemical shifts are given on the δ scale (ppm). Coupling constants (*J*) are given in Hz. The multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), and m (multiplet). Assignments of proton, carbon, and nitrogen resonances were performed by standard 2D NMR techniques (¹H–¹H COSY, ¹H–¹³C HSQC, ¹H–¹³C HMBC, ¹H–¹⁵N HMBC).

A time-of-flight (TOF) mass spectrometer equipped with a double orthogonal electrospray source at atmospheric pressure ionization (ESI) coupled to an HPLC instrument was used for recording HRMS spectra. Elemental analyses were performed with a CHNS/O analyzer. IR spectra were obtained with an ATR as a solid sample support. Melting points were determined on a Kofler micro hot stage instrument. The reactions were monitored by TLC on TLC-CARDS silica gel, 220–440 mesh.

Diffraction data for **3Bf** were collected at 150 K with a dual source using an Atlas detector and equipped with mirror-monochromated Cu Kα radiation (λ = 1.54184 Å) (University of Ljubljana). Crystal structures of **3Aa** and **3Ca** were measured at 140(2) K using a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation source (Freie Universität Berlin). The data for **3Bf** were processed by using CrysAlis PRO.⁴¹ The data collection strategy for **3Aa** and **3Ca** was evaluated by using Smart software. Data were recorded using standard ω-scan techniques, and the data were reduced and scaled using Saint+ software. The structures were solved by direct methods⁴² and refined by a full-matrix least-squares procedure based on *F*² using SHELXL-97.⁴³ All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. CCDC 978664, 969025, and 978665 contain CIF files for the **3Bf**, **3Aa**, and **3Ca**, respectively. These data can be obtained free of charge from www.ccdc.cam.ac.uk/data_requests/cif. Due to refinement problems, the deuterium atom in **3Bf** was refined as a normal hydrogen atom.

General Procedure for the Preparation of 3Aa–g and 3Ba–f.

A mixture of the triazolium salt **1Aa–g** or **1Ba–f** and Ag₂O in acetonitrile was purged with argon gas and stirred in the dark at room temperature for Time 1 (Table 1 or 2). After the addition of [Ru(η⁶-p-cymene)Cl₂]₂ the stirring was continued for 2 h (Time 2) and filtered through Celite. The solvent was removed in vacuo, and the residue was crystallized from chloroform (1–2 mL) with slow addition of hexane to give the pure **3Aa–g** or **3Ba–f**. For quantities used in the above procedure and analytical and spectral data of **3Aa–g** and **3Ba–f**, see below.

3Aa (*R* = *H*). Triazolium salt **1Aa** (38.6 mg, 0.10 mmol), Ag₂O (34.5 mg, 0.15 mmol), acetonitrile (4 mL), Time 1 = 3 days, [Ru(η⁶-p-cymene)Cl₂]₂ (30.6 mg, 0.05 mmol). Yellow solid (**3Aa**, 56.0 mg, 86%).

*R*_f(CH₂Cl₂/MeOH 10/1) = 0.2. Mp: 69–71 °C. IR: 2966, 1615, 1474, 1255, 1223, 1150, 1029, 779, 704, 636 cm^{−1}. ¹H NMR (500 MHz, CDCl₃): δ 0.97 (d, *J* = 6.9 Hz, 3H, (CH₃)₂CH), 1.05 (d, *J* = 6.9 Hz, 3H, (CH₃)₂CH), 1.99 (s, 3H, CH₃^{Cym}), 2.53 (dsept, *J* = 6.9 Hz, 1H, (CH₃)₂CH), 4.30 (s, 3H, CH₃–N-3), 5.11 (d, *J* = 5.9 Hz, 1H, ArH^{Cym}), 5.46 (dd, *J* = 6.2, 0.7 Hz, 1H, ArH^{Cym}), 5.64 (d, *J* = 5.8 Hz, 1H, ArH^{Cym}), 5.67 (d, *J* = 5.9 Hz, 1H, ArH^{Cym}), 7.70–7.66 (m, 4H, H-5', H-3'', H-4'', H-5''), 7.93–7.91 (m, 2H, H-2'', H-6''), 8.18–8.14 (m, 2H, H-3', H-4'), 9.35 (d, *J* = 5.6 Hz, 1H, H-6'). ¹³C NMR (126 MHz, CDCl₃): δ 18.7 (CH₃^{Cym}), 21.7 ((CH₃)₂CH), 22.5 ((CH₃)₂CH), 31.1 ((CH₃)₂CH), 38.5 (CH₃–N-3), 84.4 (Ar^{Cym}), 85.8 (Ar^{Cym}), 87.7 (Ar^{Cym}), 90.2 (Ar^{Cym}), 101.6 (Ar^{Cym}), 108.7 (Ar^{Cym}), 114.3 (C-3'), 126.3 (C-5'), 126.4 (C-1''), 129.5 (C-3'', C-5''), 130.7 (C-2'', C-6''), 131.2 (C-4''), 141.2 (C-4'), 147.6 (C-4), 150.3 (C-2'), 156.0 (C-6'), 169.5 (C-5). ¹⁵N NMR (51 MHz, CDCl₃): δ 226 (N-1'), 240 (N-3), 264 (N-1), 334 (N-2). ¹⁹F NMR (471 MHz, CDCl₃): δ −78.2 (s, 3F, TfO[−]). HRMS (ESI⁺): calcd for C₂₄H₂₆ClN₄Ru⁺ [M]⁺ 507.0890, found 507.0887. Anal. Calcd for C₂₅H₂₆ClF₃N₄O₃RuS·2H₂O: C, 43.38; H, 4.37; N, 8.10. Found: C, 43.12; H, 3.71; N, 8.08.

3Ab (*R* = *Me*). Triazolium salt **1Ab** (40.0 mg, 0.10 mmol), Ag₂O (34.5 mg, 0.15 mmol), acetonitrile (4 mL), Time 1 = 2 days, [Ru(η⁶-p-cymene)Cl₂]₂ (30.6 mg, 0.05 mmol). Yellow solid (**3Ab**, 64.0 mg, 96%). *R*_f(CH₂Cl₂/MeOH 10/1) = 0.3. Mp: 66–68 °C. IR: 2963, 2926, 1616, 1480, 1255, 1223, 1151, 1029, 832, 779, 754, 635 cm^{−1}. ¹H NMR (500 MHz, CDCl₃): δ 0.95 (d, *J* = 6.9 Hz, 3H, (CH₃)₂CH), 1.04 (d, *J* = 6.9 Hz, 3H, (CH₃)₂CH), 2.01 (s, 3H, CH₃^{Cym}), 2.54–2.50 (m, 4H, CH₃, (CH₃)₂CH), 4.29 (s, 3H, CH₃–N-3), 5.07 (d, *J* = 6.0 Hz, 1H, ArH^{Cym}), 5.50 (d, *J* = 6.1 Hz, 1H, ArH^{Cym}), 5.62 (d, *J* = 6.0 Hz, 1H, ArH^{Cym}), 5.71 (d, *J* = 6.1 Hz, 1H, ArH^{Cym}), 7.48 (d, *J* = 7.8 Hz, 2H, H-3'', H-5''), 7.68 (dt, *J* = 6.3, 1.6 Hz, H-5'), 7.77 (d, *J* = 8.0 Hz, 2H, H-2'', H-6''), 8.15–8.12 (m, 2H, H-3', H-4'), 9.40 (d, *J* = 5.5 Hz, 1H, H-6'). ¹³C NMR (126 MHz, CDCl₃): δ 18.8 (CH₃^{Cym}), 21.7 (CH₃–C-4''), 21.8 ((CH₃)₂CH), 22.5 ((CH₃)₂CH), 31.1 ((CH₃)₂CH), 38.4 (CH₃–N-3), 83.6 (Ar^{Cym}), 85.9 (Ar^{Cym}), 87.6 (Ar^{Cym}), 90.4 (Ar^{Cym}), 102.7 (Ar^{Cym}), 108.6 (Ar^{Cym}), 114.1 (C-3'), 123.2 (C-1''), 126.6 (C-5'), 130.2 (C-3'', C-5''), 130.5 (C-2'', C-6''), 141.2 (C-4'), 141.6 (C-4''), 147.7 (C-4), 150.1 (C-2'), 156.3 (C-6'), 169.5 (C-5). ¹⁵N NMR (51 MHz, CDCl₃): δ 226 (N-1'), 240 (N-3), 334 (N-2). ¹⁹F NMR (471 MHz, CDCl₃): δ −78.2 (s, 3F, TfO[−]). HRMS (ESI⁺): calcd for C₂₅H₂₈ClN₄Ru⁺ [M]⁺ 521.1046, found 521.1040. Anal. Calcd for C₂₆H₂₈ClF₃N₄O₃RuS·2H₂O: C, 44.22; H, 4.57; N, 7.93. Found: C, 43.96; H, 3.85; N, 7.61.

3Ac (*R* = *OMe*). Triazolium salt **1Ac** (41.6 mg, 0.10 mmol), Ag₂O (34.5 mg, 0.15 mmol), MeCN (4 mL), Time 1 = 5 days, [Ru(η⁶-p-cymene)Cl₂]₂ (30.6 mg, 0.05 mmol). Yellow solid (**3Ac**, 63.0 mg, 92%). *R*_f(CH₂Cl₂/MeOH 10/1) = 0.3. Mp: 76–78 °C. IR: 2963, 1614, 1478, 1253, 1223, 1150, 1029, 843, 779, 754, 636 cm^{−1}. ¹H NMR (500 MHz, CDCl₃): δ 0.97 (d, *J* = 7.0 Hz, 3H, (CH₃)₂CH), 1.05 (d, *J* = 6.9 Hz, 3H, (CH₃)₂CH), 2.01 (s, 3H, CH₃^{Cym}), 2.54 (dsept, *J* = 6.9 Hz, 1H, (CH₃)₂CH), 3.95 (s, 3H, OCH₃), 4.28 (s, 3H, CH₃–N-3), 5.09 (d, *J* = 6.0 Hz, 1H, ArH^{Cym}), 5.48 (dd, *J* = 6.2, 0.7 Hz, 1H, ArH^{Cym}), 5.65 (d, *J* = 6.0 Hz, 1H, ArH^{Cym}), 5.71 (d, *J* = 5.9 Hz, 1H, ArH^{Cym}), 7.19 (d, *J* = 8.9 Hz, 2H, H-3'', H-5''), 7.67 (ddd, *J* = 6.5, 5.8, 2.2 Hz, H-5'), 7.83 (d, *J* = 8.6 Hz, 2H, H-2'', H-6''), 8.17–8.12 (m, 2H, H-3', H-4'), 9.36 (d, *J* = 5.5 Hz, 1H, H-6'). ¹³C NMR (126 MHz, CDCl₃): δ 18.8 (CH₃^{Cym}), 21.8 ((CH₃)₂CH), 22.5 ((CH₃)₂CH), 31.1 ((CH₃)₂CH), 38.4 (CH₃–N-3), 55.6 (OCH₃), 83.8 (Ar^{Cym}), 85.9 (Ar^{Cym}), 87.6 (Ar^{Cym}), 90.4 (Ar^{Cym}), 102.2 (Ar^{Cym}), 108.6 (Ar^{Cym}), 114.2 (C-3'), 114.9 (C-3'', C-5''), 118.1 (C-1''), 126.4 (C-5'), 132.2 (C-2'', C-6''), 141.2 (C-4'), 147.6 (C-4), 150.3 (C-2'), 156.1 (C-6'), 161.7 (C-4''), 169.3 (C-5). ¹⁵N NMR (51 MHz, CDCl₃): δ 226 (N-1'), 240 (N-3), 264 (N-1), 334 (N-2). ¹⁹F NMR (471 MHz, CDCl₃): δ −78.2 (s, 3F, TfO[−]). HRMS (ESI⁺): calcd for C₂₅H₂₈ClN₄ORu⁺ [M]⁺ 537.0995, found 537.0987. Anal. Calcd for C₂₆H₂₈ClF₃N₄O₄RuS·H₂O: C, 44.35; H, 4.29; N, 7.96. Found: C, 44.58; H, 3.81; N, 7.56.

3Ad (*R* = *CN*). Triazolium salt **1Ad** (41.1 mg, 0.10 mmol), Ag₂O (34.5 mg, 0.15 mmol), acetonitrile (4 mL), Time 1 = 2 days, [Ru(η⁶-p-cymene)Cl₂]₂ (30.6 mg, 0.05 mmol). Yellow solid (**3Ad**, 62.0 mg, 91%). *R*_f(CH₂Cl₂/MeOH 10/1) = 0.4. Mp: 112–114 °C. IR: 3128, 2966, 2320, 1723, 1615, 1417, 1324, 1258, 1147, 1029, 826, 784, 742, 636 cm^{−1}. ¹H NMR (500 MHz, CDCl₃): δ 0.97 (d, *J* = 6.9 Hz, 3H,

(CH₃)₂CH), 1.03 (d, *J* = 6.9 Hz, 3H, (CH₃)₂CH), 1.98 (s, 3H, CH₃^{Cym}), 2.52 (dsept, *J* = 6.9 Hz, 1H, (CH₃)₂CH), 4.34 (s, 3H, CH₃-N-3), 5.08 (d, *J* = 6.3 Hz, 1H, ArH^{Cym}), 5.45 (d, *J* = 6.3 Hz, 1H, ArH^{Cym}), 5.70 (t, *J* = 5.6 Hz, 2H, ArH^{Cym}), 7.66 (dt, *J* = 5.5, 3.4 Hz, H-5'), 7.98 (d, *J* = 8.5 Hz, 2H, H-3', H-5''), 8.22–8.17 (m, 4H, H-4', H-3', H-2'', H-6''), 9.28 (d, *J* = 5.7 Hz, 1H, H-6'). ¹³C NMR (126 MHz, CDCl₃): δ 18.6 (CH₃^{Cym}), 21.7 ((CH₃)₂CH), 22.5 ((CH₃)₂CH), 31.1 ((CH₃)₂CH), 38.9 (CH₃-N-3), 85.0 (Ar^{Cym}), 86.4 (Ar^{Cym}), 87.2 (Ar^{Cym}), 90.7 (Ar^{Cym}), 100.9 (Ar^{Cym}), 108.7 (Ar^{Cym}), 114.5 (C-3'), 114.9 (C-4''), 117.8 (CN), 126.3 (C-5'), 131.1 (C-1''), 131.9 (C-2'', C-6''), 133.0 (C-3'', C-5''), 141.5 (C-4'), 146.1 (C-4), 150.3 (C-2'), 155.6 (C-6'), 170.1 (C-5). ¹⁵N NMR (51 MHz, CDCl₃): δ 225 (N-1'), 241 (N-3), 264 (N-1), 336 (N-2). ¹⁹F NMR (471 MHz, CDCl₃): δ -78.3 (s, 3F, TfO⁻). HRMS (ESI⁺): calcd for C₂₅H₂₅ClN₃Ru⁺ [M]⁺ 532.0842, found 532.0835. Anal. Calcd for C₂₆H₂₅ClF₃N₃O₃RuS·1.5H₂O: C, 44.10; H, 3.99; N, 9.89. Found: C, 43.56; H, 3.41; N, 9.53.

3Ae (*R* = CF₃). Triazolium salt **1Ae** (45.4 mg, 0.10 mmol), Ag₂O (34.5 mg, 0.15 mmol), acetonitrile (4 mL), Time 1 = 2 days, [Ru(η⁶-p-cymene)Cl₂]₂ (30.6 mg, 0.05 mmol). Yellow solid (**3Ae**, 64.7 mg, 89%). R_f(CH₂Cl₂/MeOH 10/1) = 0.4. Mp: 76–78 °C. IR: 2966, 1729, 1616, 1481, 1324, 1256, 1224, 1156, 1069, 1029, 1015, 855, 779, 694, 637 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 0.96 (d, *J* = 6.9 Hz, 3H, (CH₃)₂CH), 1.04 (d, *J* = 6.9 Hz, 3H, (CH₃)₂CH), 1.97 (s, 3H, CH₃^{Cym}), 2.53 (dsept, *J* = 6.9 Hz, 1H, (CH₃)₂CH), 4.33 (s, 3H, CH₃-N-3), 5.11 (d, *J* = 6.1 Hz, 1H, ArH^{Cym}), 5.44 (d, *J* = 6.3 Hz, 1H, ArH^{Cym}), 5.69 (d, *J* = 6.6 Hz, 2H, ArH^{Cym}), 7.66 (q, *J* = 4.9 Hz, H-5'), 7.95 (d, *J* = 8.2 Hz, 2H, H-3', H-5''), 8.18 (t, *J* = 4.2 Hz, 4H, H-4', H-3', H-2'', H-6''), 9.31 (d, *J* = 5.6 Hz, 1H, H-6'). ¹³C NMR (126 MHz, CDCl₃): δ 18.6 (CH₃^{Cym}), 21.7 ((CH₃)₂CH), 22.4 ((CH₃)₂CH), 31.1 ((CH₃)₂CH), 38.7 (CH₃-N-3), 85.0 (Ar^{Cym}), 86.0 (Ar^{Cym}), 87.6 (Ar^{Cym}), 90.3 (Ar^{Cym}), 101.1 (Ar^{Cym}), 108.7 (Ar^{Cym}), 114.4 (C-3'), 123.6 (q, *J* = 273 Hz, CF₃), 126.3 (C-5'), 126.4 (q, *J* = 4 Hz, C-3'', C-5''), 130.2 (C-1''), 131.6 (C-2'', C-6''), 133.1 (q, *J* = 33 Hz, C-4''), 141.4 (C-4'), 146.4 (C-4), 150.3 (C-2'), 155.8 (C-6'), 169.8 (C-5). ¹⁵N NMR (51 MHz, CDCl₃): δ 226 (N-1'), 241 (N-3), 264 (N-1), 336 (N-2). ¹⁹F NMR (471 MHz, CDCl₃): δ -62.9 (s, 3F, CF₃), -78.3 (s, 3F, TfO⁻). HRMS (ESI⁺): calcd for C₂₅H₂₅ClF₃N₃Ru⁺ [M]⁺ 575.0763, found 575.0758. Anal. Calcd for C₂₆H₂₅ClF₃N₃O₃RuS·H₂O: C, 42.08; H, 3.67; N, 7.55. Found: C, 41.89; H, 3.48; N, 7.15.

3Af (*R* = Br). Triazolium salt **1Af** (46.5 mg, 0.10 mmol), Ag₂O (34.5 mg, 0.15 mmol), acetonitrile (4 mL), Time 1 = 2 days, [Ru(η⁶-p-cymene)Cl₂]₂ (30.6 mg, 0.05 mmol). Yellow solid (**3Af**, 71.0 mg, 97%). R_f(CH₂Cl₂/MeOH 10/1) = 0.3. Mp: 69–71 °C. IR: 2965, 1614, 1471, 1255, 1223, 1150, 1069, 1028, 1009, 838, 778, 753, 635 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 0.99 (d, *J* = 6.9 Hz, 3H, (CH₃)₂CH), 1.06 (d, *J* = 6.9 Hz, 3H, (CH₃)₂CH), 1.99 (s, 3H, CH₃^{Cym}), 2.54 (dsept, *J* = 6.9 Hz, 1H, (CH₃)₂CH), 4.30 (s, 3H, CH₃-N-3), 5.12 (d, *J* = 6.1 Hz, 1H, ArH^{Cym}), 5.45 (d, *J* = 6.3 Hz, 1H, ArH^{Cym}), 5.70 (t, *J* = 4.7 Hz, 2H, ArH^{Cym}), 7.65 (q, *J* = 5.0 Hz, H-5'), 7.83 (d, *J* = 8.6 Hz, 2H, H-3', H-5''), 7.87 (d, *J* = 8.2 Hz, 2H, H-2'', H-6''), 8.16 (d, *J* = 4.0 Hz, 2H, H-4', H-3'), 9.30 (d, *J* = 5.6 Hz, 1H, H-6'). ¹³C NMR (126 MHz, CDCl₃): δ 18.7 (CH₃^{Cym}), 21.8 ((CH₃)₂CH), 22.5 ((CH₃)₂CH), 31.1 ((CH₃)₂CH), 38.6 (CH₃-N-3), 84.7 (Ar^{Cym}), 86.0 (Ar^{Cym}), 87.6 (Ar^{Cym}), 90.3 (Ar^{Cym}), 101.2 (Ar^{Cym}), 108.8 (Ar^{Cym}), 114.4 (C-3'), 125.3 (C-1''), 125.9 (C-4''), 126.3 (C-5'), 132.5 (C-2'', C-6''), 132.8 (C-3'', C-5''), 141.3 (C-4'), 146.7 (C-4), 150.4 (C-2'), 155.7 (C-6'), 169.5 (C-5). ¹⁵N NMR (51 MHz, CDCl₃): δ 226 (N-1'), 241 (N-3), 335 (N-2). ¹⁹F NMR (471 MHz, CDCl₃): δ -78.3 (s, 3F, TfO⁻). HRMS (ESI⁺): calcd for C₂₄H₂₅BrClN₃Ru⁺ [M]⁺ 586.9995, found 586.9970. Anal. Calcd for C₂₅H₂₅BrClF₃N₃O₃RuS·2H₂O: C, 38.94; H, 3.79; N, 7.27. Found: C, 38.50; H, 3.25; N, 6.95.

3Ag (*R* = NO₂). Triazolium salt **1Ag** (43.1 mg, 0.10 mmol), Ag₂O (34.5 mg, 0.15 mmol), acetonitrile (4 mL), Time 1 = 2 days, [Ru(η⁶-p-cymene)Cl₂]₂ (30.6 mg, 0.05 mmol). Yellow solid (**3Ag**, 59.5 mg, 85%). R_f(CH₂Cl₂/MeOH 10/1) = 0.6. Mp: 107–109 °C. IR: 2967, 1605, 1571, 1522, 1475, 1345, 1257, 1223, 1151, 1029, 866, 854, 779, 636 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 0.99 (d, *J* = 6.9 Hz, 3H, (CH₃)₂CH), 1.04 (d, *J* = 6.9 Hz, 3H, (CH₃)₂CH), 1.99 (s, 3H, CH₃^{Cym}), 2.54 (dsept, *J* = 6.9 Hz, 1H, (CH₃)₂CH), 4.36 (s, 3H, CH₃-N-3), 5.10 (d, *J* = 6.0 Hz, 1H, ArH^{Cym}), 5.45 (d, *J* = 6.2 Hz, 1H, ArH^{Cym}), 5.72 (dd, *J* = 10.4, 6.2 Hz, 2H, ArH^{Cym}), 7.66 (td, *J* = 5.7, 3.1 Hz, H-5'), 8.20 (dd, *J* =

4.2, 2.0 Hz, 2H, H-4', H-3'), 8.31 (d, *J* = 8.0 Hz, 2H, H-2'', H-6''), 8.53 (d, *J* = 8.9 Hz, 2H, H-3'', H-5''), 9.26 (d, *J* = 5.5 Hz, 1H, H-6'). ¹³C NMR (126 MHz, CDCl₃): δ 18.6 (CH₃^{Cym}), 21.7 ((CH₃)₂CH), 22.7 ((CH₃)₂CH), 31.1 ((CH₃)₂CH), 39.0 (CH₃-N-3), 85.1 (Ar^{Cym}), 86.4 (Ar^{Cym}), 87.2 (Ar^{Cym}), 90.7 (Ar^{Cym}), 100.7 (Ar^{Cym}), 108.8 (Ar^{Cym}), 114.6 (C-3'), 124.4 (C-3'', C-5''), 126.3 (C-5'), 132.4 (C-2'', C-6''), 132.9 (C-1''), 141.4 (C-4'), 145.8 (C-4), 149.3 (C-4''), 150.4 (C-2'), 155.5 (C-6'), 170.2 (C-5). ¹⁵N NMR (51 MHz, CDCl₃): δ 225 (N-1'), 241 (N-3), 264 (N-1), 337 (N-2), 367 (NO₂). ¹⁹F NMR (471 MHz, CDCl₃): δ -78.3 (s, 3F, TfO⁻). HRMS (ESI⁺): calcd for C₂₄H₂₅ClN₃O₃Ru⁺ [M]⁺ 552.0740, found 552.0729. Anal. Calcd for C₂₅H₂₅ClF₃N₃O₃RuS·1.5H₂O: C, 41.24; H, 3.88; N, 9.52. Found: C, 41.03; H, 3.46; N, 9.35.

3Ba (*R* = H). Triazolium salt **1Ba** (32.4 mg, 0.10 mmol), Ag₂O (34.5 mg, 0.15 mmol), acetonitrile (4 mL), Time 1 = 4 days, [Ru(η⁶-p-cymene)Cl₂]₂ (30.6 mg, 0.05 mmol). Orange-yellow solid (**3Ba**, 58.0 mg, 78%). R_f(CH₂Cl₂/MeOH 10/1) = 0.3. Mp: 101–103 °C. IR: 2967, 1617, 1498, 1460, 1326, 1286, 1050, 1033, 772, 749, 697, 671 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.00 (d, *J* = 7.0 Hz, 3H, (CH₃)₂CH), 1.08 (d, *J* = 6.9 Hz, 3H, (CH₃)₂CH), 4.36 (s, 3H, CH₃-N-3), 4.86 (d, *J* = 5.8 Hz, 1H, ArH^{Cym}), 5.29 (d, *J* = 6.1 Hz, 1H, ArH^{Cym}), 5.48 (dd, *J* = 12.8, 6.0 Hz, 2H, ArH^{Cym}), 7.46 (ddd, *J* = 7.2, 5.7, 1.5 Hz, 1H, H-5'), 7.74–7.69 (m, 3H, H-3'', H-4'', H-5''), 8.09–8.02 (m, 4H, H-3', H-4', H-2'', H-6''), 9.39 (d, *J* = 5.5 Hz, 1H, H-6'). ¹³C NMR (100 MHz, CDCl₃): δ 18.8 (CH₃^{Cym}), 21.6 ((CH₃)₂CH), 22.7 ((CH₃)₂CH), 31.2 ((CH₃)₂CH), 39.1 (CH₃-N-3), 82.9 (Ar^{Cym}), 86.0 (Ar^{Cym}), 86.7 (Ar^{Cym}), 90.2 (Ar^{Cym}), 103.0 (Ar^{Cym}), 108.5 (Ar^{Cym}), 112.9 (C-3'), 125.4 (C-5'), 125.6 (C-2'', C-6''), 129.8 (C-3'', C-5''), 131.2 (C-4''), 138.2 (C-1''), 139.5 (C-4'), 143.8 (C-4), 148.6 (C-2'), 157.3 (C-6'), 174.0 (C-5). ¹⁵N NMR (51 MHz, CDCl₃): δ 231 (N-3), 243 (N-1'), 262 (N-1'), 353 (N-2). ¹⁹F NMR (471 MHz, CDCl₃): δ -152.6 (d, *J* = 25 Hz, 4F, BF₄⁻). ¹¹B NMR (160 MHz, CDCl₃): δ -1.2 (s, 1B, BF₄⁻). HRMS (ESI⁺): calcd for C₂₄H₂₆ClN₃Ru⁺ [M]⁺ 507.0884, found 507.0883. Anal. Calcd for C₂₄H₂₆BClF₄N₃Ru·2.5H₂O: C, 45.12; H, 4.89; N, 8.77. Found: C, 45.09; H, 4.00; N, 8.64.

3Bb (*R* = CH₃). Triazolium salt **1Bb** (33.8 mg, 0.10 mmol), Ag₂O (34.5 mg, 0.15 mmol), acetonitrile (4 mL), Time 1 = 3 days, [Ru(η⁶-p-cymene)Cl₂]₂ (30.6 mg, 0.05 mmol). Yellow solid (**3Bb**, 49.4 mg, 81%). R_f(CH₂Cl₂/MeOH 10/1) = 0.3. Mp: 112–114 °C. IR: 2965, 1616, 1515, 1459, 1325, 1049, 1033, 779, 750, 708 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 0.95 (d, *J* = 7.0 Hz, 3H, (CH₃)₂CH), 1.03 (d, *J* = 6.9 Hz, 3H, (CH₃)₂CH), 2.03 (s, 3H, CH₃^{Cym}), 2.50 (dsept, *J* = 6.9 Hz, 1H, (CH₃)₂CH), 2.54 (s, 3H, CH₃), 4.58 (s, 3H, CH₃-N-3), 4.81 (d, *J* = 5.8 Hz, 1H, ArH^{Cym}), 5.31 (d, *J* = 6.7 Hz, 1H, ArH^{Cym}), 5.42 (d, *J* = 5.9 Hz, 1H, ArH^{Cym}), 5.54 (d, *J* = 6.1 Hz, 1H, ArH^{Cym}), 7.47–7.43 (m, 3H, H-5', H-3'', H-5''), 7.90 (d, *J* = 8.9 Hz, 2H, H-2'', H-6''), 8.06–7.99 (m, 2H, H-3', H-4'), 9.41 (d, *J* = 5.5 Hz, 1H, H-6'). ¹³C NMR (100 MHz, CDCl₃): δ 18.9 (CH₃^{Cym}), 21.5 (CH₃-C-4''), 21.6 ((CH₃)₂CH), 22.7 ((CH₃)₂CH), 31.2 ((CH₃)₂CH), 39.3 (CH₃-N-3), 82.5 (Ar^{Cym}), 86.0 (Ar^{Cym}), 86.8 (Ar^{Cym}), 90.3 (Ar^{Cym}), 103.6 (Ar^{Cym}), 108.3 (Ar^{Cym}), 121.9 (C-3'), 125.2 (C-2'', C-6''), 125.5 (C-5'), 130.3 (C-3'', C-5''), 135.7 (C-1''), 139.5 (C-4''), 141.7 (C-4''), 143.8 (C-4), 148.5 (C-2'), 157.4 (C-6'), 173.8 (C-5). ¹⁵N NMR (51 MHz, CDCl₃): δ 230 (N-3), 242 (N-1'), 263 (N-1), 353 (N-2). ¹⁹F NMR (471 MHz, CDCl₃): δ -152.6 (d, *J* = 25 Hz, 4F, BF₄⁻). ¹¹B NMR (160 MHz, CDCl₃): δ -1.0 (s, 1B, BF₄⁻). HRMS (ESI⁺): calcd for C₂₅H₂₈ClN₃Ru⁺ [M]⁺ 521.1046, found 521.1036. Anal. Calcd for C₂₅H₂₈BClF₄N₃Ru·1.5H₂O: C, 47.30; H, 4.92; N, 8.82. Found: C, 47.16; H, 4.51; N, 9.27.

3Bc (*R* = OCH₃). Triazolium salt **1Bc** (35.4 mg, 0.10 mmol), Ag₂O (34.5 mg, 0.15 mmol), acetonitrile (4 mL), Time 1 = 6 days, [Ru(η⁶-p-cymene)Cl₂]₂ (30.6 mg, 0.05 mmol). Yellow solid (**3Bc**, 56.8 mg, 91%). R_f(CH₂Cl₂/MeOH 10/1) = 0.3. Mp: 111–113 °C. IR: 2965, 1616, 1514, 1461, 1324, 1050, 1029, 842, 779, 751, 604 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 0.96 (d, *J* = 7.0 Hz, 3H, (CH₃)₂CH), 1.04 (d, *J* = 6.8 Hz, 3H, (CH₃)₂CH), 2.02 (s, 3H, CH₃^{Cym}), 2.46 (dsept, *J* = 7.0 Hz, 1H, (CH₃)₂CH), 3.96 (s, 3H, OCH₃), 4.57 (s, 3H, CH₃-N-3), 4.83 (d, *J* = 5.8 Hz, 1H, ArH^{Cym}), 5.30 (dd, *J* = 6.1, 1.3 Hz, 1H, ArH^{Cym}), 5.45 (d, *J* = 5.2 Hz, 1H, ArH^{Cym}), 5.54 (d, *J* = 6.9 Hz, 1H, ArH^{Cym}), 7.15 (d, *J* = 8.9 Hz, 2H, H-3'', H-5''), 7.43 (ddd, *J* = 7.2, 5.6, 1.7 Hz, 1H, H-5'), 7.94 (d, *J* =

8.9 Hz, 2H, H-2'', H-6''), 8.05–8.00 (m, 2H, H-3', H-4'), 9.38 (d, $J = 5.2$ Hz, 1H, H-6'). ^{13}C NMR (126 MHz, CDCl_3): δ 18.8 (CH_3^{Cym}), 21.6 ($(\text{CH}_3)_2\text{CH}$), 22.7 ($(\text{CH}_3)_2\text{CH}$), 31.2 ($(\text{CH}_3)_2\text{CH}$), 39.2 ($\text{CH}_3\text{-N-3}$), 55.9 (OCH_3), 82.5 (Ar^{Cym}), 85.9 (Ar^{Cym}), 86.8 (Ar^{Cym}), 90.2 (Ar^{Cym}), 103.2 (Ar^{Cym}), 108.4 (Ar^{Cym}), 114.8 (C-3'), 121.9 (C-3'), 125.4 (C-5'), 126.9 (C-2'', C-6''), 131.0 (C-1''), 139.5 (C-4'), 143.6 (C-4), 148.6 (C-2'), 157.3 (C-6'), 161.5 (C-4''), 173.8 (C-5). ^{15}N NMR (51 MHz, CDCl_3): δ 230 (N-3), 243 (N-1'), 262 (N-1), 353 (N-2). ^{19}F NMR (471 MHz, CDCl_3): δ -152.5 (d, $J = 25$ Hz, 4F, BF_4^-). ^{11}B NMR (160 MHz, CDCl_3): δ -1.1 (s, 1B, BF_4^-). HRMS (ESI+): calcd for $\text{C}_{25}\text{H}_{28}\text{ClN}_4\text{ORu}^+ [\text{M}]^+$ 537.0995, found 537.0991. Anal. Calcd for $\text{C}_{25}\text{H}_{28}\text{BrClF}_4\text{N}_4\text{ORu}\cdot\text{H}_2\text{O}$: C, 46.13; H, 4.80; N, 8.61. Found: C, 46.17; H, 4.55; N, 9.00.

3Bd ($R = \text{CN}$). Triazolium salt **1Bd** (34.9 mg, 0.10 mmol), Ag_2O (34.5 mg, 0.15 mmol), acetonitrile (4 mL), Time 1 = 7 days, $[\text{Ru}(\eta^6\text{-p-cymene})\text{Cl}_2]_2$ (30.6 mg, 0.05 mmol). Orange-yellow solid (**3Bd**, 49.0 mg, 80%). $R_f(\text{CH}_2\text{Cl}_2/\text{MeOH } 10/1) = 0.3$. Mp: 135–137 °C. IR: 2966, 2232, 1672, 1608, 1508, 1477, 1326, 1285, 1050, 1002, 853, 778, 749 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 1.05 (d, $J = 7.0$ Hz, 3H, $(\text{CH}_3)_2\text{CH}$), 1.11 (d, $J = 7.1$ Hz, 3H, $(\text{CH}_3)_2\text{CH}$), 2.00 (s, 3H, CH_3^{Cym}), 2.56 (dsept, $J = 6.9$ Hz, 1H, $(\text{CH}_3)_2\text{CH}$), 4.63 (s, 3H, $\text{CH}_3\text{-N-3}$), 4.93 (d, $J = 5.9$ Hz, 1H, ArH^{Cym}), 5.27 (d, $J = 6.2$ Hz, 1H, ArH^{Cym}), 5.47 (d, $J = 5.9$ Hz, 1H, ArH^{Cym}), 5.60 (d, $J = 5.9$ Hz, 1H, ArH^{Cym}), 7.47 (ddd, $J = 7.2, 5.7, 1.6$ Hz, 1H, H-5'), 8.00 (d, $J = 8.6$ Hz, 2H, H-3'', H-5''), 8.07 (td, $J = 7.7, 1.4$ Hz, 2H, H-3', H-4'), 8.35 (d, $J = 8.6$ Hz, 2H, H-2'', H-6''), 9.33 (d, $J = 5.6$ Hz, 1H, H-6'). ^{13}C NMR (126 MHz, CDCl_3): δ 18.7 (CH_3^{Cym}), 21.6 ($(\text{CH}_3)_2\text{CH}$), 22.7 ($(\text{CH}_3)_2\text{CH}$), 31.2 ($(\text{CH}_3)_2\text{CH}$), 39.5 ($\text{CH}_3\text{-N-3}$), 83.8 (Ar^{Cym}), 86.3 (Ar^{Cym}), 86.6 (Ar^{Cym}), 90.1 (Ar^{Cym}), 101.9 (Ar^{Cym}), 109.3 (Ar^{Cym}), 115.2 (C-1''), 117.0 (CN), 121.9 (C-3'), 125.4 (C-5'), 126.6 (C-2'', C-6''), 133.7 (C-3'), 139.6 (C-4'), 141.4 (C-4''), 144.2 (C-4), 148.8 (C-2'), 157.0 (C-6'), 174.4 (C-5). ^{15}N NMR (51 MHz, CDCl_3): δ 233 (N-3), 242 (N-1'), 259 (N-1), 353 (N-2). ^{19}F NMR (471 MHz, CDCl_3): δ -152.7 (d, $J = 25$ Hz, 4F, BF_4^-). ^{11}B NMR (160 MHz, CDCl_3): δ -1.2 (s, 1B, BF_4^-). HRMS (ESI+): calcd for $\text{C}_{25}\text{H}_{25}\text{ClN}_5\text{Ru}^+ [\text{M}]^+$ 532.0842, found 532.0834. Anal. Calcd for $\text{C}_{25}\text{H}_{25}\text{BrClF}_4\text{N}_5\text{Ru}\cdot\text{H}_2\text{O}$: C, 47.15; H, 4.27; N, 11.00. Found: C, 46.88; H, 4.08; N, 10.69.

3Be ($R = \text{CF}_3$). Triazolium salt **1Be** (39.2 mg, 0.10 mmol), Ag_2O (34.5 mg, 0.15 mmol), acetonitrile (4 mL), Time 1 = 6 days, $[\text{Ru}(\eta^6\text{-p-cymene})\text{Cl}_2]_2$ (30.6 mg, 0.05 mmol). Yellow-brown solid (**3Be**, 47.3 mg, 72%). $R_f(\text{CH}_2\text{Cl}_2/\text{MeOH } 10/1) = 0.3$. Mp: 103–105 °C. IR: 2965, 1663, 1615, 1322, 1169, 1051, 1002, 856, 779, 750 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 1.00 (d, $J = 6.9$ Hz, 3H, $(\text{CH}_3)_2\text{CH}$), 1.07 (d, $J = 7.0$ Hz, 3H, $(\text{CH}_3)_2\text{CH}$), 1.99 (s, 3H, CH_3^{Cym}), 2.51 (dsept, $J = 7.0$ Hz, 1H, $(\text{CH}_3)_2\text{CH}$), 4.61 (s, 3H, $\text{CH}_3\text{-N-3}$), 4.89 (dd, $J = 6.0, 1.3$ Hz, 1H, ArH^{Cym}), 5.26 (d, $J = 6.2$ Hz, 1H, ArH^{Cym}), 5.47 (d, $J = 1.3$ Hz, 1H, ArH^{Cym}), 5.54 (d, $J = 6.0$ Hz, 1H, ArH^{Cym}), 7.46 (td, $J = 5.7, 3.0$ Hz, 1H, H-5'), 7.96 (d, $J = 8.2$ Hz, 2H, H-3'', H-5''), 8.04 (m, 2H, H-3', H-4'), 8.29 (d, $J = 8.2$ Hz, 2H, H-2'', H-6''), 9.35 (d, $J = 5.6$ Hz, 1H, H-6'). ^{13}C NMR (126 MHz, CDCl_3): δ 18.7 (CH_3^{Cym}), 21.5 ($(\text{CH}_3)_2\text{CH}$), 22.8 ($(\text{CH}_3)_2\text{CH}$), 31.2 ($(\text{CH}_3)_2\text{CH}$), 39.4 ($\text{CH}_3\text{-N-3}$), 83.7 (Ar^{Cym}), 86.1 (Ar^{Cym}), 86.9 (Ar^{Cym}), 89.8 (Ar^{Cym}), 102.0 (Ar^{Cym}), 109.4 (Ar^{Cym}), 121.9 (C-3'), 123.3 (q, $J = 273$ Hz, CF_3), 125.3 (C-5'), 126.2 (C-2'', C-6''), 127.0 (q, $J = 4$ Hz, C-3'), 133.2 (q, $J = 34$ Hz, C-4'), 139.5 (C-4'), 140.9 (C-1''), 144.1 (C-4), 148.8 (C-2'), 157.0 (C-6'), 174.2 (C-5). ^{15}N NMR (51 MHz, CDCl_3): δ 232 (N-3), 243 (N-1'), 260 (N-1), 354 (N-2). ^{19}F NMR (471 MHz, CDCl_3): δ -62.7 (s, 3F, CF_3), -152.9 (d, $J = 25$ Hz, 4F, BF_4^-). ^{11}B NMR (160 MHz, CDCl_3): δ -1.2 (s, 1B, BF_4^-). HRMS (ESI+): calcd for $\text{C}_{25}\text{H}_{25}\text{ClF}_6\text{N}_4\text{Ru}^+ [\text{M}]^+$ 575.0763, found 575.0758. Anal. Calcd for $\text{C}_{25}\text{H}_{25}\text{BrClF}_6\text{N}_4\text{Ru}\cdot 2\text{H}_2\text{O}$: C, 43.03; H, 4.19; N, 8.03. Found: C, 42.59; H, 3.75; N, 8.48.

3Bf ($R = \text{Br}$). Triazolium salt **1Bf** (40.2 mg, 0.10 mmol), Ag_2O (34.5 mg, 0.15 mmol), acetonitrile (4 mL), Time 1 = 3 days, $[\text{Ru}(\eta^6\text{-p-cymene})\text{Cl}_2]_2$ (30.6 mg, 0.05 mmol). Yellow solid (**3Bf**, 58.3 mg, 87%). $R_f(\text{CH}_2\text{Cl}_2/\text{MeOH } 10/1) = 0.3$. Mp: 117–119 °C. IR: 2964, 1616, 1492, 1480, 1326, 1050, 998, 839, 779, 750, 709, 695 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 1.01 (d, $J = 6.9$ Hz, 3H, $(\text{CH}_3)_2\text{CH}$), 1.08 (d, $J = 6.8$ Hz, 3H, $(\text{CH}_3)_2\text{CH}$), 2.00 (s, 3H, CH_3^{Cym}), 2.51 (dsept, $J = 6.9$ Hz, 1H, $(\text{CH}_3)_2\text{CH}$), 4.59 (s, 3H, $\text{CH}_3\text{-N-3}$), 4.88 (dd, $J = 6.0, 1.3$ Hz, 1H, ArH^{Cym}), 5.26 (dd, $J = 6.3, 0.7$ Hz, 1H, ArH^{Cym}), 5.47 (dd, $J = 6.0, 1.3$

Hz, 1H, ArH^{Cym}), 5.53 (dd, $J = 6.1, 1.4$ Hz, 1H, ArH^{Cym}), 7.44 (ddd, $J = 6.8, 5.8, 2.3$ Hz, 1H, H-5'), 7.81 (d, $J = 8.7$ Hz, 2H, H-3'', H-5''), 8.00 (m, 4H, H-3', H-4', H-2'', H-6''), 9.34 (dd, $J = 5.7, 1.3$ Hz, 1H, H-6'). ^{13}C NMR (126 MHz, CDCl_3): δ 18.7 (CH_3^{Cym}), 21.5 ($(\text{CH}_3)_2\text{CH}$), 22.8 ($(\text{CH}_3)_2\text{CH}$), 31.2 ($(\text{CH}_3)_2\text{CH}$), 39.3 ($\text{CH}_3\text{-N-3}$), 83.2 (Ar^{Cym}), 86.0 (Ar^{Cym}), 86.9 (Ar^{Cym}), 89.9 (Ar^{Cym}), 102.2 (Ar^{Cym}), 109.4 (Ar^{Cym}), 121.9 (C-3'), 125.2 (C-5'), 140.5 (C-1''), 127.2 (C-2'', C-6''), 133.0 (C-3'), 137.1 (C-4''), 139.4 (C-4'), 144.0 (C-4), 148.9 (C-2'), 156.9 (C-6'), 174.0 (C-5). ^{15}N NMR (51 MHz, CDCl_3): δ 231 (N-3), 243 (N-1'), 260 (N-1), 354 (N-2). ^{19}F NMR (471 MHz, CDCl_3): δ -153.0 (d, $J = 25$ Hz, 4F, BF_4^-). ^{11}B NMR (160 MHz, CDCl_3): δ -1.2 (s, 1B, BF_4^-). HRMS (ESI+): calcd for $\text{C}_{24}\text{H}_{25}\text{BrClF}_4\text{N}_4\text{Ru}^+ [\text{M}]^+$ 584.9995, found 584.9971. Anal. Calcd for $\text{C}_{24}\text{H}_{25}\text{BBrClF}_4\text{N}_4\text{Ru}\cdot\text{H}_2\text{O}$: C, 41.73; H, 3.94; N, 8.11. Found: C, 41.42; H, 3.46; N, 8.06.

General Procedure for the Preparation of 3Ca–e,h. A mixture of the triazolium salt **1Ca–e,h** and Ag_2O in acetonitrile was purged with argon gas and stirred in the dark at 60 °C for Time 1 (Table 3). The reaction mixture was cooled to room temperature. $[\text{Ru}(\eta^6\text{-p-cymene})\text{Cl}_2]_2$ was added, and the reaction mixture was stirred for Time 2 (Table 3) and then filtered through Celite. The solvent was removed in vacuo, and the residue was subjected to flash column chromatography on silica using hexane and a mixture of acetone and dichloromethane (1/1) as eluent. The products **3Ca–e,h** were recrystallized from chloroform (1–2 mL) with slow addition of hexane. For quantities used in the above procedure and analytical and spectral data of **3Ca–e,h**, see below.

3Ca ($R = \text{H}$). Triazolium salt **1Ca** (39.6 mg, 0.10 mmol), Ag_2O (34.5 mg, 0.15 mmol), acetonitrile (4 mL), Time 1 = 4 h, $[\text{Ru}(\eta^6\text{-p-cymene})\text{Cl}_2]_2$ (30.6 mg, 0.05 mmol), Time 2 = 2 days. Yellow solid (**3Ca**, 33.0 mg, 50%). $R_f(\text{CH}_2\text{Cl}_2/\text{MeOH } 10/1) = 0.4$. Mp: 103–105 °C. IR: 2922, 2851, 1608, 1442, 1304, 1162, 1077, 1023, 830, 770, 702 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 0.82 (d, $J = 7.0$ Hz, 3H, $(\text{CH}_3)_2\text{CH}$), 1.13 (d, $J = 6.9$ Hz, 3H, $(\text{CH}_3)_2\text{CH}$), 1.64 (s, 3H, CH_3^{Cym}), 2.25–2.19 (m, 1H, $(\text{CH}_3)_2\text{CH}$), 3.95 (s, 3H, $\text{CH}_3\text{-N-3}$), 5.25 (dd, $J = 6.1, 0.6$ Hz, 1H, ArH^{Cym}), 5.39 (dd, $J = 6.1, 0.6$ Hz, 1H, ArH^{Cym}), 5.50–5.47 (m, 2H, ArH^{Cym} , CH_2), 5.69 (dd, $J = 6.1, 0.6$ Hz, 1H, ArH^{Cym}), 5.82 (d, $J = 16.0$ Hz, 1H, CH_2), 7.46–7.43 (m, 1H, H-5'), 7.58 (d, $J = 6.4, 3.1$ Hz, 4H, H-3', H-3'', H-4'', H-5''), 7.84 (dd, $J = 6.6, 3.0$ Hz, 2H, H-2'', H-6''), 7.92 (dt, $J = 7.7, 1.5$ Hz, 1H, H-4'), 9.53 (dd, $J = 5.7, 1.2$ Hz, 1H, H-6'). ^{13}C NMR (126 MHz, CDCl_3): δ 18.1 (CH_3^{Cym}), 21.9 ($(\text{CH}_3)_2\text{CH}$), 22.8 ($(\text{CH}_3)_2\text{CH}$), 31.2 ($(\text{CH}_3)_2\text{CH}$), 37.2 ($\text{CH}_3\text{-N-3}$), 56.9 (CH_2), 86.0 (Ar^{Cym}), 86.3 (Ar^{Cym}), 86.6 (Ar^{Cym}), 89.1 (Ar^{Cym}), 97.6 (Ar^{Cym}), 107.3 (Ar^{Cym}), 124.8 (C-5'), 125.4 (C-3'), 126.9 (C-1''), 128.8 (C-2'', C-6''), 130.4 (C-4''), 131.5 (C-3', C-5''), 139.5 (C-4'), 148.7 (C-4), 154.6 (C-2'), 159.2 (C-6'), 159.6 (C-5). ^{15}N NMR (51 MHz, CDCl_3): δ 235 (N-1'), 237 (N-3), 246 (N-1), 345 (N-2). ^{19}F NMR (471 MHz, CDCl_3): δ -73.5 (d, $J = 713$ Hz, 6F, PF_6^-). ^{31}P NMR (202 MHz, CDCl_3): δ -144.6 (sept, $J = 713$ Hz, 1P, PF_6^-). HRMS (ESI+): calcd for $\text{C}_{25}\text{H}_{28}\text{ClN}_4\text{Ru}^+ [\text{M}]^+$ 521.1046, found 521.1040. Anal. Calcd for $\text{C}_{25}\text{H}_{28}\text{ClF}_6\text{N}_4\text{PRu}\cdot 2\text{H}_2\text{O}$: C, 42.77; H, 4.59; N, 7.98. Found: C, 42.99; H, 4.32; N, 7.50.

3Cb ($R = \text{Me}$). Triazolium salt **1Cb** (40.9 mg, 0.10 mmol), Ag_2O (34.5 mg, 0.15 mmol), acetonitrile (4 mL), Time 1 = 8 h, $[\text{Ru}(\eta^6\text{-p-cymene})\text{Cl}_2]_2$ (30.6 mg, 0.05 mmol), Time 2 = 2 days. Yellow solid (**3Cb**, 30.6 mg, 45%). $R_f(\text{CH}_2\text{Cl}_2/\text{MeOH } 10/1) = 0.6$. Mp: 118–120 °C. IR: 2922, 2852, 1609, 1443, 1305, 1240, 1162, 1077, 1020, 833, 765, 692 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 0.86 (d, $J = 7.0$ Hz, 3H, $(\text{CH}_3)_2\text{CH}$), 1.13 (d, $J = 6.9$ Hz, 3H, $(\text{CH}_3)_2\text{CH}$), 1.68 (s, 3H, CH_3^{Cym}), 2.28 (dsept, $J = 6.9$ Hz, 1H, $(\text{CH}_3)_2\text{CH}$), 2.46 (s, 3H, CH_3), 3.94 (s, 3H, $\text{CH}_3\text{-N-3}$), 5.25 (d, $J = 6.0$ Hz, 1H, ArH^{Cym}), 5.37 (dd, $J = 6.1, 0.6$ Hz, 1H, ArH^{Cym}), 5.49–5.45 (m, 2H, ArH^{Cym} , CH_2), 5.66 (dd, $J = 6.0, 0.7$ Hz, 1H, ArH^{Cym}), 5.80 (d, $J = 16.0$ Hz, 1H, CH_2), 7.38 (d, $J = 7.9$ Hz, 2H, H-3'', H-5''), 7.45–7.42 (m, 1H, H-5'), 7.58 (d, $J = 7.6$ Hz, 1H, H-3'), 7.71 (d, $J = 8.1$ Hz, 2H, H-2'', H-6''), 7.92 (dt, $J = 7.7, 1.5$ Hz, 1H, H-4'), 9.51 (dd, $J = 5.8, 1.2$ Hz, 1H, H-6'). ^{13}C NMR (126 MHz, CDCl_3): δ 18.2 (CH_3^{Cym}), 21.5 ($\text{CH}_3\text{-C-4''}$), 22.0 ($(\text{CH}_3)_2\text{CH}$), 22.7 ($(\text{CH}_3)_2\text{CH}$), 31.2 ($(\text{CH}_3)_2\text{CH}$), 37.2 ($\text{CH}_3\text{-N-3}$), 56.9 (CH_2), 85.9 (Ar^{Cym}), 85.9 (Ar^{Cym}), 86.7 (Ar^{Cym}), 88.8 (Ar^{Cym}), 97.9 (Ar^{Cym}), 107.8 (Ar^{Cym}), 123.9 (C-1''), 124.8 (C-5'), 125.4 (C-3'), 129.5 (C-3', C-5''), 131.3 (C-2'', C-6''), 139.4 (C-4'), 140.6 (C-4''), 148.9 (C-4), 154.6 (C-2'), 159.1 (C-6'), 159.6 (C-5). ^{15}N NMR (51 MHz, CDCl_3): δ 235 (N-

1'), 237 (N-3), 245 (N-1), 345 (N-2). ^{19}F NMR (471 MHz, CDCl_3): δ -73.4 (d, J = 713 Hz, 6F, PF_6). ^{31}P NMR (202 MHz, CDCl_3): δ -144.5 (sept, J = 713 Hz, 1P, PF_6). HRMS (ESI+): calcd for $\text{C}_{26}\text{H}_{30}\text{ClN}_4\text{Ru}^+ [\text{M}]^+$ 535.1203, found 535.1194. Anal. Calcd for $\text{C}_{26}\text{H}_{30}\text{ClF}_6\text{N}_4\text{PRu} \cdot 0.4\text{C}_6\text{H}_{14}$: C, 47.74; H, 5.02; N, 7.84. Found: C, 47.93; H, 4.65; N, 7.46.

3Cc ($R = \text{OMe}$). Triazolium salt **1Cc** (42.6 mg, 0.10 mmol), Ag_2O (34.5 mg, 0.15 mmol), acetonitrile (4 mL), Time 1 = 10 h, $[\text{Ru}(\eta^6\text{-p-cymene})\text{Cl}_2]_2$ (30.6 mg, 0.05 mmol), Time 2 = 4 days. Yellow solid (**3Cc**, 27.0 mg, 40%). $R_f(\text{CH}_2\text{Cl}_2/\text{MeOH } 10/1) = 0.6$. Mp: 117–119 °C. IR: 2921, 1611, 1541, 1487, 1441, 1303, 1253, 1181, 1078, 1024, 833, 767, 693 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 0.88 (d, J = 7.0 Hz, 3H, $(\text{CH}_3)_2\text{CH}$), 1.14 (d, J = 6.9 Hz, 3H, $(\text{CH}_3)_2\text{CH}$), 1.71 (s, 3H, CH_3^{Cym}), 2.31 (dsept, J = 6.9 Hz, 1H, $(\text{CH}_3)_2\text{CH}$), 3.89 (s, 3H, OCH_3), 3.94 (s, 3H, $\text{CH}_3\text{-N-3}$), 5.25 (d, J = 6.0 Hz, 1H, ArH^{Cym}), 5.38 (dd, J = 6.2, 0.8 Hz, 1H, ArH^{Cym}), 5.47–5.43 (m, 2H, ArH^{Cym} , CH_2), 5.66 (dd, J = 5.9, 0.8 Hz, 1H, ArH^{Cym}), 5.80 (d, J = 16.0 Hz, 1H, CH_2), 7.09 (d, J = 8.1 Hz, 2H, H-3", H-5"), 7.45–7.42 (m, 1H, H-5'), 7.58 (d, J = 7.5 Hz, 1H, H-3'), 7.77 (d, J = 8.1 Hz, 2H, H-2", H-6"), 7.92 (dt, J = 7.7, 1.5 Hz, 1H, H-4'), 9.52 (dd, J = 5.7, 1.2 Hz, 1H, H-6'). ^{13}C NMR (126 MHz, CDCl_3): δ 18.3 (CH_3^{Cym}), 22.0 ($(\text{CH}_3)_2\text{CH}$), 22.8 ($(\text{CH}_3)_2\text{CH}$), 31.2 ($(\text{CH}_3)_2\text{CH}$), 37.1 ($\text{CH}_3\text{-N-3}$), 55.5 (OCH_3), 56.8 (CH_2), 85.8 (Ar^{Cym}), 85.8 (Ar^{Cym}), 86.6 (Ar^{Cym}), 89.0 (Ar^{Cym}), 97.8 (Ar^{Cym}), 107.9 (Ar^{Cym}), 114.2 (C-2", C-6"), 118.8 (C-1"), 124.8 (C-5'), 125.4 (C-3'), 132.9 (C-3", C-5"), 139.4 (C-4'), 148.7 (C-4), 154.6 (C-2'), 159.1 (C-6'), 159.6 (C-5), 161.1 (C-4"). ^{15}N NMR (51 MHz, CDCl_3): δ 236 (N-1'), 237 (N-3), 246 (N-1), 345 (N-2). ^{19}F NMR (471 MHz, CDCl_3): δ -73.2 (d, J = 713 Hz, 6F, PF_6). ^{31}P NMR (202 MHz, CDCl_3): δ -144.5 (sept, J = 713 Hz, 1P, PF_6). HRMS (ESI+): calcd for $\text{C}_{26}\text{H}_{30}\text{ClN}_4\text{ORu}^+ [\text{M}]^+$ 551.1152, found 551.1143. Anal. Calcd for $\text{C}_{26}\text{H}_{30}\text{ClF}_6\text{N}_4\text{OPRu} \cdot 1.5\text{H}_2\text{O}$: C, 43.19; H, 4.60; N, 7.75. Found: C, 43.30; H, 4.47; N, 7.14.

3Cd ($R = \text{CN}$). Triazolium salt **1Cd** (42.2 mg, 0.10 mmol), Ag_2O (34.5 mg, 0.15 mmol), acetonitrile (4 mL), Time 1 = 3 h, $[\text{Ru}(\eta^6\text{-p-cymene})\text{Cl}_2]_2$ (30.6 mg, 0.05 mmol), Time 2 = 2 days. Yellow solid (**3Cd**, 26.0 mg, 38%). $R_f(\text{CH}_2\text{Cl}_2/\text{MeOH } 10/1) = 0.8$. Mp: 132–134 °C. IR: 2964, 2230, 1610, 1440, 1401, 1305, 1278, 1240, 1161, 1076, 1019, 831, 764, 691 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 0.83 (d, J = 6.9 Hz, 3H, $(\text{CH}_3)_2\text{CH}$), 1.14 (d, J = 6.9 Hz, 3H, $(\text{CH}_3)_2\text{CH}$), 1.66 (s, 3H, CH_3^{Cym}), 2.22 (dsept, J = 6.8 Hz, 1H, $(\text{CH}_3)_2\text{CH}$), 3.97 (s, 3H, $\text{CH}_3\text{-N-3}$), 5.25 (d, J = 6.0 Hz, 1H, ArH^{Cym}), 5.40 (d, J = 6.0 Hz, 1H, ArH^{Cym}), 5.44 (d, J = 15.9 Hz, 1H, CH_2), 5.56 (d, J = 6.1 Hz, 1H, ArH^{Cym}), 5.72 (d, J = 5.9 Hz, 1H, ArH^{Cym}), 5.85 (d, J = 15.9 Hz, 1H, CH_2), 7.47 (t, J = 6.7 Hz, 1H, H-5'), 7.62 (d, J = 7.6 Hz, 1H, H-3'), 7.89 (d, J = 8.2 Hz, 2H, H-3", H-5"), 7.95 (dt, J = 7.6, 0.8 Hz, 1H, H-4'), 8.10 (d, J = 8.2 Hz, 2H, H-2", H-6"), 9.52 (d, J = 5.3 Hz, 1H, H-6'). ^{13}C NMR (126 MHz, CDCl_3): δ 18.2 (CH_3^{Cym}), 21.6 ($(\text{CH}_3)_2\text{CH}$), 23.0 ($(\text{CH}_3)_2\text{CH}$), 31.4 ($(\text{CH}_3)_2\text{CH}$), 37.5 ($\text{CH}_3\text{-N-3}$), 56.9 (CH_2), 85.9 (Ar^{Cym}), 86.5 (Ar^{Cym}), 86.6 (Ar^{Cym}), 89.5 (Ar^{Cym}), 97.4 (Ar^{Cym}), 107.8 (Ar^{Cym}), 114.3 (CN), 118.0 (C-1"), 125.0 (C-5'), 125.5 (C-3'), 131.7 (C-4"), 132.4 (C-3", C-5"), 132.7 (C-2", C-6"), 139.6 (C-4'), 147.0 (C-4), 154.5 (C-2'), 159.2 (C-6'), 160.3 (C-5). ^{15}N NMR (51 MHz, CDCl_3): δ 235 (N-1'), 237 (N-3), 247 (N-1), 347 (N-2). ^{19}F NMR (471 MHz, (v): δ -73.4 (d, J = 713 Hz, 6F, PF_6). ^{31}P NMR (202 MHz, CDCl_3): δ -144.6 (sept, J = 713 Hz, 1P, PF_6). HRMS (ESI+): calcd for $\text{C}_{26}\text{H}_{27}\text{ClN}_4\text{Ru}^+ [\text{M}]^+$ 546.0999, found 546.0989. Anal. Calcd for $\text{C}_{26}\text{H}_{27}\text{ClF}_6\text{N}_4\text{PRu} \cdot \text{H}_2\text{O}$: C, 44.04; H, 4.12; N, 9.88. Found: C, 44.34; H, 3.80; N, 9.34.

3Ce ($R = \text{CF}_3$). Triazolium salt **1Ce** (46.4 mg, 0.10 mmol), Ag_2O (34.5 mg, 0.15 mmol), acetonitrile (4 mL), Time 1 = 2 h, $[\text{Ru}(\eta^6\text{-p-cymene})\text{Cl}_2]_2$ (30.6 mg, 0.05 mmol), Time 2 = 2 days. Yellow solid (**3Ce**, 33.0 mg, 45%). $R_f(\text{CH}_2\text{Cl}_2/\text{MeOH } 10/1) = 0.7$. Mp: 116–118 °C. IR: 2960, 2922, 1609, 1439, 1406, 1325, 1239, 1167, 1126, 1070, 1017, 832, 766, 691 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 0.79 (d, J = 7.0 Hz, 3H, $(\text{CH}_3)_2\text{CH}$), 1.12 (d, J = 6.9 Hz, 3H, $(\text{CH}_3)_2\text{CH}$), 1.63 (s, 3H, CH_3^{Cym}), 2.11 (dsept, J = 6.9 Hz, 1H, $(\text{CH}_3)_2\text{CH}$), 3.97 (s, 3H, $\text{CH}_3\text{-N-3}$), 5.30 (d, J = 6.0 Hz, 1H, ArH^{Cym}), 5.38 (d, J = 6.0 Hz, 1H, ArH^{Cym}), 5.45 (d, J = 15.9 Hz, 1H, CH_2), 5.54 (d, J = 6.1 Hz, 1H, ArH^{Cym}), 5.74 (d, J = 6.0 Hz, 1H, ArH^{Cym}), 5.85 (d, J = 15.9 Hz, 1H, CH_2), 7.46 (t, J = 6.7 Hz, 1H, H-5'), 7.62 (d, J = 7.6 Hz, 1H, H-3'), 7.86 (d, J = 8.2 Hz, 2H, H-3", H-5"), 7.95 (dt, J = 7.7, 1.4 Hz, 1H, H-4'), 8.07 (d, J = 8.1 Hz, 2H, H-2", H-6"), 9.53 (dd, J = 5.6, 0.9 Hz, 1H, H-6'). ^{13}C

NMR (126 MHz, CDCl_3): δ 18.1 (CH_3^{Cym}), 21.9 ($(\text{CH}_3)_2\text{CH}$), 22.6 ($(\text{CH}_3)_2\text{CH}$), 31.2 ($(\text{CH}_3)_2\text{CH}$), 37.4 ($\text{CH}_3\text{-N-3}$), 56.9 (CH_2), 85.7 (Ar^{Cym}), 87.2 (Ar^{Cym}), 87.5 (Ar^{Cym}), 88.3 (Ar^{Cym}), 97.3 (Ar^{Cym}), 107.3 (Ar^{Cym}), 123.7 (q, J = 273 Hz, CF_3), 124.9 (C-5'), 125.5 (C-3'), 125.7 (q, J = 4 Hz, C-3", C-5"), 130.7 (C-1"), 132.5 (q, J = 33 Hz, C-4"), 132.4 (C-2", C-6"), 139.6 (C-4'), 147.4 (C-4), 154.5 (C-2'), 159.2 (C-6'), 160.1 (C-5). ^{15}N NMR (51 MHz, CDCl_3): δ 235 (N-1'), 237 (N-3), 247 (N-1), 347 (N-2). ^{19}F NMR (471 MHz, CDCl_3): δ -63.0 (s, 3F, CF_3), -73.4 (d, J = 713 Hz, 6F, PF_6). ^{31}P NMR (202 MHz, CDCl_3): δ -144.6 (sept, J = 712 Hz, 1P, PF_6). HRMS (ESI+): calcd for $\text{C}_{26}\text{H}_{27}\text{ClF}_6\text{N}_4\text{Ru}^+ [\text{M}]^+$ 589.0920, found 589.0911. Anal. Calcd for $\text{C}_{26}\text{H}_{27}\text{ClF}_6\text{N}_4\text{PRu} \cdot 0.2\text{C}_6\text{H}_{14}$: C, 43.49; H, 4.00; N, 7.46. Found: C, 43.39; H, 3.73; N, 7.39.

3Ch ($R = \text{Cl}$). Triazolium salt **1Ch** (44.0 mg, 0.10 mmol), Ag_2O (34.5 mg, 0.15 mmol), acetonitrile (4 mL), Time 1 = 9 h, $[\text{Ru}(\eta^6\text{-p-cymene})\text{Cl}_2]_2$ (30.6 mg, 0.05 mmol), Time 2 = 2 days. Yellow solid (**3Ch**, 32.0 mg, 42%). $R_f(\text{CH}_2\text{Cl}_2/\text{MeOH } 10/1) = 0.7$. Mp: 122–124 °C. IR: 2963, 2925, 2238, 1607, 1476, 1437, 1305, 1239, 1162, 1093, 1077, 1014, 831, 763, 691 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 0.84 (d, J = 7.0 Hz, 3H, $(\text{CH}_3)_2\text{CH}$), 1.12 (d, J = 6.9 Hz, 3H, $(\text{CH}_3)_2\text{CH}$), 1.70 (s, 3H, CH_3^{Cym}), 2.24 (dsept, J = 6.9 Hz, 1H, $(\text{CH}_3)_2\text{CH}$), 3.95 (s, 3H, $\text{CH}_3\text{-N-3}$), 5.24 (dd, J = 6.1, 1.3 Hz, 1H, ArH^{Cym}), 5.36 (dd, J = 6.2, 1.5 Hz, 1H, ArH^{Cym}), 5.41 (d, J = 15.9 Hz, 1H, CH_2), 5.48 (dd, J = 6.2, 1.4 Hz, 1H, ArH^{Cym}), 5.67 (dd, J = 6.1, 1.4 Hz, 1H, ArH^{Cym}), 5.81 (d, J = 15.9 Hz, 1H, CH_2), 7.43 (ddd, J = 7.4, 5.8, 1.4 Hz, 1H, H-5'), 7.54 (d, J = 8.6 Hz, 2H, H-3", H-5"), 7.59 (d, J = 9.5 Hz, 1H, H-3'), 7.82 (d, J = 8.5 Hz, 2H, H-2", H-6"), 7.91 (td, J = 7.7, 1.6 Hz, 1H, H-4'), 9.49 (dd, J = 5.8, 1.6 Hz, 1H, H-6'). ^{13}C NMR (126 MHz, CDCl_3): δ 18.2 (CH_3^{Cym}), 21.8 ($(\text{CH}_3)_2\text{CH}$), 22.8 ($(\text{CH}_3)_2\text{CH}$), 31.2 ($(\text{CH}_3)_2\text{CH}$), 37.2 ($\text{CH}_3\text{-N-3}$), 56.8 (CH_2), 85.8 (Ar^{Cym}), 86.3 (Ar^{Cym}), 86.8 (Ar^{Cym}), 97.6 (Ar^{Cym}), 107.9 (Ar^{Cym}), 124.9 (C-1"), 125.4 (C-5'), 125.5 (C-3'), 129.1 (C-3", C-5"), 133.1 (C-2", C-6"), 136.8 (C-4"), 139.6 (C-4'), 147.6 (C-4), 154.5 (C-2'), 159.2 (C-6'), 159.9 (C-5). ^{15}N NMR (51 MHz, CDCl_3): δ 235 (N-1'), 237 (N-3), 246 (N-1), 346 (N-2). ^{19}F NMR (471 MHz, CDCl_3): δ -73.3 (d, J = 713 Hz, 6F, PF_6). ^{31}P NMR (202 MHz, CDCl_3): δ -144.6 (sept, J = 713 Hz, 1P, PF_6). HRMS (ESI+): calcd for $\text{C}_{25}\text{H}_{27}\text{Cl}_2\text{N}_4\text{Ru}^+ [\text{M}]^+$ 555.0656, found 555.0651.

tert-Butyl 2-Methoxy-5-bromobenzoperoxoate (7b). $R_f(\text{light petroleum/ethyl acetate } 5/1) = 0.5$. ^1H NMR (300 MHz, CDCl_3): δ 1.42 (s, 9H, *t*-Bu), 3.90 (s, 3H, OCH_3), 6.88 (d, J = 8.9 Hz, ArH), 7.59 (dd, J = 8.9, 2.6 Hz, ArH), 7.81 (d, J = 2.6 Hz, ArH). HRMS (ESI+): calcd for $\text{C}_{12}\text{H}_{16}\text{BrO}_4^+ [\text{M} + \text{H}]^+$ 303.0226, found 303.0225.

■ ASSOCIATED CONTENT

Supporting Information

Figures, tables, and CIF files giving N-1, N-2, and N-3 chemical and coordination shifts, crystallographic data for complexes **3Aa**, **3Bf**, and **3Ca**, and NMR spectra of compounds **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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