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Synthesis, Structure, and Antiproliferative Activity of Ruthenium(II) Arene Complexes with N,O-Chelating Pyrazolone-Based β-Ketoamine Ligands

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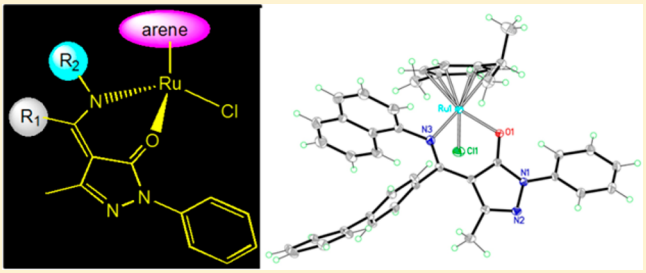
Supporting Information

ABSTRACT: Novel ruthenium half-sandwich complexes containing (N,O)-bound pyrazolone-based β-ketoamine ligands have been prepared, and the solid-state structures of one ligand and five complexes have been determined by single-crystal X-ray diffraction. Some of the complexes display moderate cytotoxicity toward the human ovarian cancer cell lines A2780 and A2780cisR, the latter line having acquired resistance to cisplatin.



INTRODUCTION

Metal-based compounds are among the most widely used chemotherapeutic agents and continue to play an important role in the treatment of many cancers since the discovery of cisplatin.[1] Although platinum-based compounds are among the most successful anticancer drugs employed in the clinic, they are not without problems.[2] In the search for anticancer agents containing metals other than platinum, ruthenium compounds have become promising alternatives to platinum-based drugs.[3]

Certain ruthenium complexes display specific activities against different cancers and favorable toxicity and clearance properties, and two Ru^{III} compounds are presently undergoing clinical trials.[4] It has been proposed that their mode of action involves in vivo reduction to the more reactive Ru^{II} species, and this feature has led, at least in part, to the growing interest in the medicinal properties of organometallic Ru^{II} arene complexes.[5] The hydrophobic arene ligand is thought to facilitate the diffusion through the lipophilic cell membrane,[6] and the remaining three coordination sites comprise various ligands including those that are relatively labile, to eventually allow direct binding to a target biomolecule and more stable ligands which help to modulate biological and pharmacological properties of the compound.[7] Nevertheless, the molecular targets and mechanism of action of ruthenium(II)−arene compounds are poorly understood.[8] A recent study on two prototypical ruthenium−arene agents, the cytotoxic antiprimary tumor compound [Ru(cym)(ethylene-diamine)Cl]PF_6 and the relatively non-cytotoxic antimetastasis compound [Ru(cym)-(1,3,5-triaza-7-phosphaadamantane)Cl_2] (RAPTA-C), revealed quite distinct targets for the two compounds: the former targets the DNA of chromatin, while the latter preferentially forms adducts on the histone proteins.[9] In addition, arene−ruthenium complexes containing σ-bonded ligands with aromatic side arms[10] or with π-bonded arenes[11] may bind DNA also by intercalation, where the planar part of the compounds undergo noncovalent stacking interactions with DNA base pairs. Intercalative interactions between metal complexes and DNA introduce new mechanisms for attack on DNA and new concepts for developing structure−activity relationships.[12]

Recently, we have shown that Ru^{II} arene complexes containing pyrazolone-based β-ketoamine ligands are cytotoxic to cancer cells including cisplatin-resistant cell lines, where minor changes to the ligands result in considerable changes to their cytotoxicity.[13] These ligands represent an interesting class in order to fine-tune the anticancer properties of the ruthenium arene unit. On the basis of the observed results we have hypothesized that tethering a DNA intercalator to the ruthenium(II) arene unit may allow DNA intercalation, enhancing the cytotoxic effect of the compounds. Herein, we present a systematic investigation of half-sandwich Ru^{II} complexes with pyrazolone-based β-ketoamine ligands with respect to their antiproliferative activity on human ovarian cancer cells.

RESULTS AND DISCUSSION

Condensation of 4-acyl-5-pyrazolones (HQ′) with 1-naphthylamine or aniline affords the proligands (HL′; $HL^{biph,ph}$ = (4*Z*)-3-methyl-4-((phenylamino)(4-biphenyl)methylene)-1-phenyl-1*H*-pyrazol-5(4*H*)-one, $HL^{biph,naph}$ = (4*Z*)-3-methyl-4-((naph-

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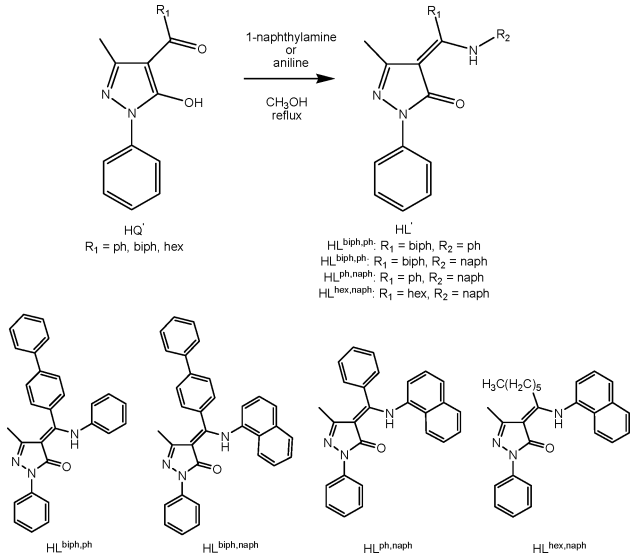
thalen-1-ylamino)(4-biphenyl)methylene)-1-phenyl-1*H*-pyrazol-5(4*H*)-one, $HL^{ph,naph}$ = (4*Z*)-3-methyl-4-((naphthalen-1-ylamino)(phenyl)methylene)-1-phenyl-1*H*-pyrazol-5(4*H*)-one, $HL^{hex,naph}$ = (4*Z*)-3-methyl-4-(1-(naphthalen-1-ylamino) heptylidene)-1-phenyl-1*H*-pyrazol-5(4*H*)-one) in high yield (Scheme 1).

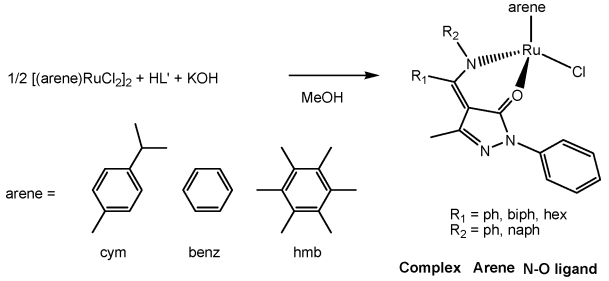
Scheme 1. Synthesis of Proligands HL′



Compared to the ketoamine proligands previously investigated,[13] the novel proligands HL′ are insoluble in water.

Complexes **1**−**9** were prepared by reacting $[Ru(arene)Cl_2]_2$ and the appropriate deprotonate ligand in methanol (Scheme 2). All complexes are air-stable in the solid state and in solution

Scheme 2. Synthesis of Complexes 1−9



Complex	Arene	N-O ligand
1	cym	$L^{biph,ph}$
2	benz	$L^{biph,ph}$
3	hmb	$L^{biph,ph}$
4	cym	$L^{biph,naph}$
5	cym	$L^{ph,naph}$
6	benz	$L^{ph,naph}$
7	hmb	$L^{ph,naph}$
8	cym	$L^{hex,naph}$
9	hmb	$L^{hex,naph}$

and are highly soluble in most organic solvents, but insoluble in water. Conductivity measurements indicate a slight dissociation of the chloride ligand in DMSO at room temperature. The extent of chloride loss increases with temperature, and at 353 K dissociation is almost complete. The IR spectra of **1**−**9** show the typical shift of the ν(C═O) vibrations to lower frequency upon coordination of the β-ketoamine proligands to the ruthenium(II) ion. The ^{1}H NMR spectra of **1**−**9** display distinct changes in frequency for the resonances of the β-ketoamine protons in comparison with the equivalent protons in the free proligands. As expected, the ^{1}H NMR spectra of complexes **1**, **2**, and **3** containing the $L^{biph,ph}$ ligand display one set of signals due to unhindered rotation of the phenyl ring.

The ^{1}H NMR spectrum of **1** in $CDCl_3$ contains a doublet for each of the four *p*-cymene ring protons and two doublets corresponding to the methyl groups of the isopropyl moiety. One of the four proton resonances attributable to the *p*-cymene ring is strongly shifted to higher frequency (3.52 ppm), whereas the other three doublets are in the range 5.14−5.37 ppm, which is typical of ruthenium arene systems.[14] The above-mentioned shift of one of the aromatic protons results from the close vicinity of the phenyl group in the ammine moiety of the ligand, as confirmed from X-ray diffraction studies (see below). Also, in the ^{13}C NMR spectra of **1**, signals corresponding to four different *p*-cymene ring carbons are observed in the range 79.2−87.0 ppm together with signals that may be attributed to two different methyl groups of the isopropyl moiety at 21.2 and 23.7 ppm. A similar pattern is observed in the ^{1}H and ^{13}C NMR of **4**, **5**, and **8**, where, however, two sets of signals are detected, due to the presence of two conformers (in 1:1 ratio) in solution, differing in the orientation of the naphthyl group of the chelating ligands with respect to the cymene moiety on the Ru(II) center, as previously observed for similar compounds.[11] In the ^{1}H NMR spectra of **4**, **5**, and **8** in DMSO-d_6, over the temperature range 298−373 K, coalescence of the two sets of resonances is observed. In detail, at 298 K the aromatic protons of the *p*-cymene ring give rise to eight separate doublets (integrating 1H each) and the methyl groups of the isopropyl moiety give rise to two partially superimposed doublets. Above 363 K all the peaks attributable to the *p*-cymene ring protons broaden, and at 373 K they coalesce to form four broad resonances, presumably due to rapid isomerization between the two forms on the NMR time scale. Solutions of the complexes in $[D_6]$DMSO and D_2O were prepared and maintained at 37 °C for 7 days, and monitored by ^{1}H NMR spectroscopy. Within this period the ^{1}H NMR spectra of **1**−**9** remained unchanged. The ESI mass spectra of **1**−**9** in positive ion mode contain peaks that may be attributed to the cationic fragment $[Ru(arene)(L')]^+$, generated from loss of Cl^- ligand. Furthermore, the stability of compounds **1**, **4**, **5**, and **8** in water−methanol solution was assayed by ESI-MS and their mass spectra remained essentially constant over the entire incubation period. Only a small peak appears after 24 h, due to the formation of a small amount of the dinuclear hydrolysis product $[Ru_2(cym)_2(\mu\text{-}OCH_3)_3]^+$ (*m*/*z* 565.08), arising from β ketoamine ligand dissociation, and bridging methoxy groups from methanol molecules. However, we cannot exclude that such β ketoamine ligand dissociation may be due to the soft electrospray process, as previously reported.[15]

The crystal structures of $HL^{ph,naph}$, **1**, **4**, **5**, **8**, and **9** were determined by X-ray crystallography (see Experimental Section for details of the data collections and structure refinements). The molecular structures are shown in Figure 1, and key bond lengths and angles are given in the caption. The solid state structure of the proligand $HL^{ph,naph}$ shows an essentially planar geometry for the phenyl-pyrazolone moiety with a rather short intramolecular H-bond between the −NH and the −C═O moieties (N−H···O: 2.698(2) Å; 144(2)°), as observed in related compounds.[13,14] The orientations of the main substituents on the central partial double bond (C3−C11, 1.398(2) Å) are shown by the torsion angles between the −naphthyl and the −CNH groups (−26.6°), as well as by the dihedral angle calculated between the phenyl and the −CNH

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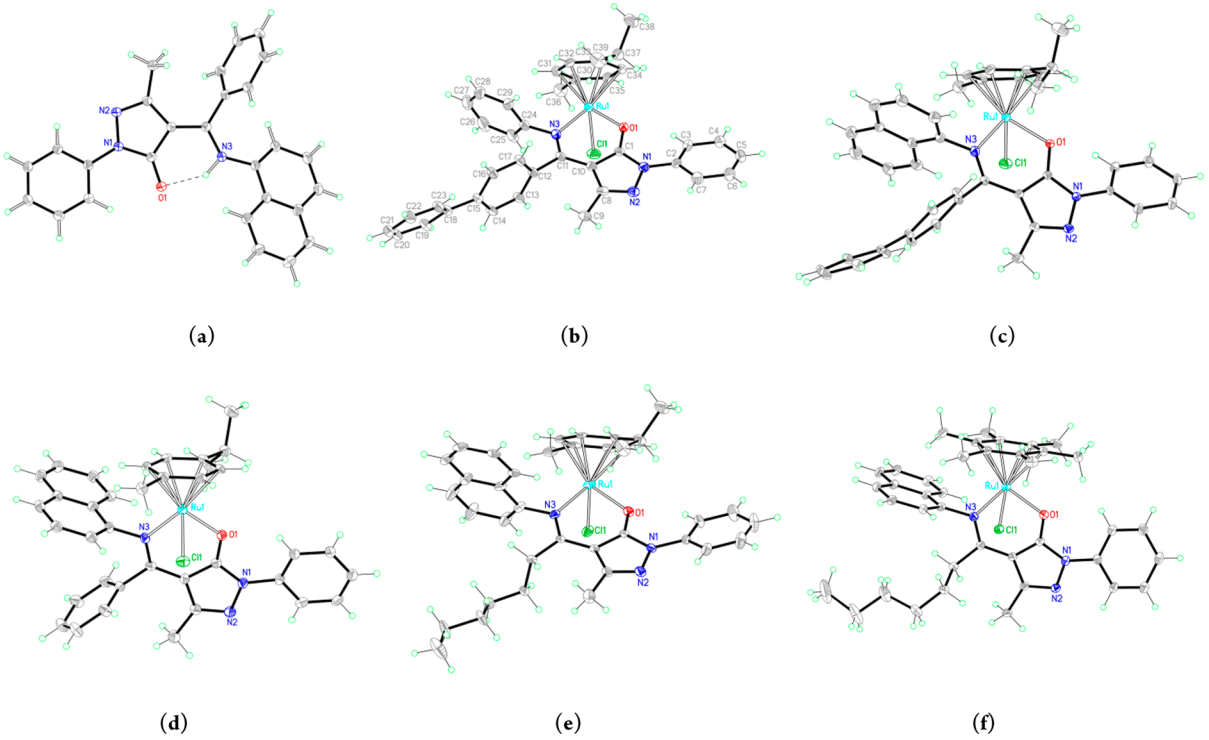

Figure 1. Molecular structures of $HL^{ph,naph}$ (a); **1**, [Ru(cym)($L^{biph,ph}$)Cl] (b); **4**, [Ru(cym)($L^{biph,naph}$)Cl] (c); **5**, [Ru(cym)($L^{ph,naph}$)Cl] (d); **8**, [Ru(cym)($L^{hex,naph}$)Cl] (e); and **9**, [Ru(hmb)($L^{hex,naph}$)Cl] (f). Selected bond lengths (Å) and angles (deg): $HL^{ph,naph}$, C1−O1 1.255(2), N1−N2 1.406(2), N3···O1 2.698(2), N3−H3···O1 144(2); **1**, Ru1−O1 2.068(4), Ru1−N3 2.130(5), Ru1−Cl1 2.412(2), O1−Ru1−N3 87.45(18), O1−Ru1−Cl1 85.05(15), N3−Ru1−Cl1 84.39(15); **4**, Ru1−O1 2.073(2), Ru1−N3 2.148(2), Ru1−Cl1 2.420(1), O1−Ru1−N3 87.81(9), O1−Ru1−Cl1 83.67(6), N3−Ru1−Cl1 87.28(8); **5**, Ru1−O1 2.083(3), Ru1−N3 2.118(3), Ru1−Cl1 2.447(1), O1−Ru1−N3 88.74(13), O1−Ru1−Cl1 84.66(9), N3−Ru1−Cl1 83.89(10); **8**, Ru1−O1 2.070(3), Ru1−N3 2.128(4), Ru1−Cl1 2.426(1), O1−Ru1−N3 88.91(13), O1−Ru1−Cl1 84.84(10), N3−Ru1−Cl1 84.43(11); **9**, Ru1−O1 2.084(5), Ru1−N3 2.164(6), Ru1−Cl1 2.444(2), O1−Ru1−N3 89.37(19), O1−Ru1−Cl1 84.61(15), N3−Ru1−Cl1 81.67(16).

moieties (−63.2°). The observed twisting of the molecule is presumably due to steric hindrance among the substituents. Complexes **1**, **4**, **5**, **8**, and **9** adopt the expected piano-stool coordination geometry around the ruthenium ion. Differences in the backbone of the ligands arise from the different substituents although they do not modify the bond distances and angles (see the figure caption) around the metal center to a large extent, and these values are comparable with those found for similar compounds.[13,16] The Ru−η^6-arene centroid distances are 1.666(3) (**1**), 1.661(1) (**4**), 1.674(2) (**5**), 1.676 (**8** which displays a disordered *p*-cymene), and 1.701(4) (**9**) Å, suggesting that the metal−arene interaction is slightly weaker for the hexamethylbenzene ring. This may also explain the rather long Ru−N bond distance (2.163(7) Å) in **9**.

CYTOTOXICITY STUDIES

The ligands and complexes were tested for their cytotoxicity to human ovarian A2780 carcinoma cells and the A2780cisR variant with acquired resistance to cisplatin. IC_{50} values of the compounds were determined after exposure of the cells to the compounds for 72 h using the MTT assay (see Experimental Section). The IC_{50} values of the compounds are listed in Table 1.

It might be expected that the ligands would be cytotoxic as the aromatic rings, i.e., phenyl, biphenyl, and naphthyl rings, could intercalate with DNA. However, the ligands are not appreciable cytotoxic with the exception of $HL^{biph,ph}$ that has an IC_{50} value of 31 ± 3 in the nonresistant A2780 cell line. Complexes **1** and **5**−**8** are significantly more cytotoxic than the ligands with the biphenyl-containing complex **1** showing the highest levels of cytotoxicity to the nonresistant A2780 cell line (IC_{50} = 7.6 ± 1.3) and **2**, also with a biphenyl ring, being most cytotoxic toward the resistant A2780cisR cell line (IC_{50} = 13 ± 1). Compounds **1** and **2** simply differ according to the nature of the η^6-arene ring, i.e., *p*-cymene in **1** and benzene in **2**. Surprisingly the hexamethylbenzene adduct is considerably less cytotoxic toward both cancer cell lines.

Table 1. Cytotoxicity of the Compounds and Cisplatin Following Exposure to the Ovarian Carcinoma Cells A2780 and A2780cisR (Cisplatin-Resistant) for 72 h

	IC_{50}, μM		
compound	A2780	A2780cisR	resistance factor
$HL^{biph,ph}$	31 ± 3	191 ± 6	6.1
$HL^{biph,naph}$	109 ± 9	261 ± 14	2.4
$HL^{ph,naph}$	65 ± 3	114 ± 10	1.8
$HL^{hex,naph}$	108 ± 6	102 ± 3	0.9
1	7.6 ± 1.3	61 ± 5	8.1
2	16.7 ± 1.2	13 ± 1	0.8
3	63.1 ± 1.2	442 ± 20	7.0
4	96 ± 4	243 ± 19	2.5
5	23 ± 2	20 ± 1	0.9
6	20 ± 1	21 ± 4	1.1
7	20 ± 1	24 ± 3	1.2
8	31 ± 2	30 ± 10	1.0
9	126 ± 14	49 ± 1	0.4
cisplatin	1.0 ± 0.2	25 ± 1	25

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In comparison to the previous series of compounds we reported,[13] in which the C atom derivatived with the biphenyl group in **1**−**4** was derivatized with a naphthyl group, IC_{50} values tend to be quite similar. However, the most cytotoxic compound from both series in the A2780 cell line is the *p*-cymene derivative with three phenyl rings attached to the bidentate N,O− ligand (IC_{50} = 7.6 ± 1.1) and the most cytotoxic compound toward the resistant A2780cisR cell line is the benzene derivative also with three phenyl rings on the bidentate N,O− ligand. Combined, these results imply that intercalative interactions do not play a significant role in mechanism of action of these types of compounds.

CONCLUSIONS

Ruthenium(II) arene complexes with pyrazolone-based *β*-ketoamine ligands containing phenyl, biphenyl, and naphthyl groups in varying positions were prepared in order to evaluate the influence of aromatic substituents on their in vitro anticancer activity. Ruthenium(II) arene compounds may coordinate directly to the DNA or histone core in chromatin, and it is known that protruding aromatic ligands may intercalate DNA.[11] However, the ligands were not cytotoxic, indicating that DNA intercalation is unlikely. Nevertheless, some of the resulting compounds are reasonably cytotoxic and, interestingly, in the A2780cisR cell line **2** is significantly more cytotoxic than cisplatin (IC_{50} values of 13 ± 1 and 25 ± 1, respectively) and **5** and **6** are marginally more cytotoxic than cisplatin to this resistant cell line. Overall, the cytotoxicity of **1**, **2**, **5**, and **6** is similar to that observed for many other series of organoruthenium compounds.

EXPERIMENTAL SECTION

Materials and Methods. The dimers $[Ru(arene)Cl_2]_2$ (arene = cym, benz, or hmb) were purchased from Aldrich. The acylpyrazolone ligands HQ^{ph}, HQ^{biph}, and HQ^{hex} were synthesized using literature methods.[17] All other materials were obtained from commercial sources and were used as received. IR spectra were recorded from 4000 to 600 cm^{-1} on a PerkinElmer Spectrum 100 FT-IR instrument. ^1H and ^{13}C NMR spectra were recorded on a 400 Mercury Plus Varian instrument operating at room temperature (400 MHz for ^1H and 100 MHz for ^{13}C) relative to TMS. Positive and negative ion electrospray mass spectra were obtained on a series 1100 MSI detector HP spectrometer using methanol as the mobile phase. Solutions (3 mg/mL) for electrospray ionization mass spectrometry (ESI-MS) were prepared using reagent-grade methanol. Masses and intensities were compared to those calculated using IsoPro Isotopic Abundance Simulator, version 2.1.28. Melting points are uncorrected and were recorded on a STMP3 Stuart scientific instrument and on a capillary apparatus. Samples for microanalysis were dried in vacuo to constant weight (20 °C, ca. 0.1 Torr) and analyzed on a Fisons Instruments 1108 CHNS-O elemental analyzer. Electrical conductivity measurements (Λ_M, reported as S cm^2 mol^{-1}) of acetonitrile and dichloromethane solutions of the complexes were recorded using a Crison CDTM 522 conductimeter at room temperature.

X-ray Crystallography. The diffraction data of compounds **4** and **8** were measured at low temperature [100(2) K] using Mo K*α* radiation on a Bruker APEX II CCD diffractometer equipped with a kappa geometry goniometer. The data sets were reduced by EvalCCD[18] and then corrected for absorption.[19] The data collections of compounds HL^{ph}, naph, **5**, and **9** were collected at low temperature [140(2) K] using Mo K*α* radiation on a mar345dtb system in combination with a Genix Hi-Flux small focus generator (*marμX* system). The data reduction was carried out by *automar*.[20] The data collection of compound **1** was performed at room temperature using Cu K*α* radiation on an Agilent Technologies SuperNova dual system in combination with an Atlas CCD detector. The data reduction was carried out by Crysalis PRO.[21]

The solutions and refinements were performed by SHELX.[22] The crystal structures were refined using full-matrix least-squares based on F^2 with all non-hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the "riding" model.

Cell Culture and Inhibition of Cell Growth. The human A2780 and A2780cisR ovarian carcinoma and HEK (human embryonic kidney) cells were obtained from the European Collection of Cell Cultures (Salisbury, U.K.). A2780 and A2780R cells were grown routinely in RPMI-1640 medium, while HEK cells were grown with DMEM medium, with 10% fetal calf serum (FCS) and antibiotics at 37 °C and 5% CO_2. Cytotoxicity was determined using the MTT assay (MTT = 3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl-2*H*-tetrazolium bromide). Cells were seeded in 96-well plates as monolayers with 100 *μ*L of cell solution (approximately 20 000 cells) per well and preincubated for 24 h in medium supplemented with 10% FCS. Compounds were prepared as DMSO solutions and then dissolved in the culture medium and serially diluted to the appropriate concentration, to give a final DMSO concentration of 0.5%. A 100 *μ*L portion of the drug solution was added to each well, and the plates were incubated for another 72 h. Subsequently, MTT (5 mg/mL solution) was added to the cells and the plates were incubated for a further 2 h. The culture medium was aspirated, and the purple formazan crystals formed by the mitochondrial dehydrogenase activity of vital cells were dissolved in DMSO. The optical density, directly proportional to the number of surviving cells, was quantified at 590 nm using a multiwell plate reader, and the fraction of surviving cells was calculated from the absorbance of untreated control cells. Evaluation is based on means from two independent experiments, each comprising three microcultures per concentration level.

Syntheses and Characterization. *$HL^{biph,ph}$*. To a solution of HQ^{biph} (1-phenyl-3-methyl-4-biphenyl-5-pyrazolone, 2.00 g, 5.64 mmol) in ethanol (75 mL) was added dropwise a solution of aniline (0.52 g, 5,64 mmol). The solution was stirred at reflux for 24 h. The solvent was removed under reduced pressure, and dichloromethane (10 mL) was added. The mixture was filtered, and *n*-hexane (20 mL) was added to the solution to form a biphase, which was stored at 4 °C. Yellow crystals were obtained and collected. The mixture was filtered and the precipitate washed with ethanol (20 mL). The yellow precipitate was recrystallized in methanol at 4 °C (2.23 g, 5.20 mmol, yield 92%). The compound is soluble in diethyl ether, alcohols, acetone, acetonitrile, DMSO, and chlorinated solvents. Mp: 175−177 °C. Anal. Calcd for $C_{29}H_{23}N_3O$: C, 81.09; H, 5.40; N, 9.78. Found: C, 80.76; H, 5.37; N, 9.59. IR (cm^{-1}): 3054w, 1615s, 1579s, 1519w *ν*(C═C; C═N). ^1H NMR ($CDCl_3$, 298 K): *δ*, 1.62 (s, 3H, C3−CH_3), 6.85 (d, 2H), 7.00−7.74 (m, 15H), 8.10 (d, 2H), 13.00 (sbr, 1H, −NH). ^{13}C NMR ($CDCl_3$, 298 K): *δ*, 16.5 (s, C3−CH_3), 101.7 (s, *C*4), 119.5, 121.0, 124.0, 124.7, 126.2, 126.9, 127.2, 127.4, 127.6, 128.4, 128.8, 129.0, 129.2, 129.3, 130.4, 137.7, 139.1, 139.6, 143.4, 148.3, 162.2, 165.9 (s, ligand $HL^{biph,ph}$). ESI-MS (−) CH_3OH (*m*/*z*, relative intensity %): 429 [100] $[L^{biph,ph}]^-$.

Ligand $HL^{biph,naph}$. The synthesis was performed as for $HL^{biph,ph}$ using 1-phenyl-3-methyl-4-biphenyl-5-pyrazolone (2.00 g, 5.64 mmol) and 1-naphthylamine (0.80 g, 5.64 mmol). The compound is soluble in diethyl ether, alcohols, acetone, acetonitrile, DMSO, and chlorinated solvents. Mp: 266−268 °C. Anal. Calcd for $C_{33}H_{25}N_3O$: C, 82.67; H, 5.21; N, 8.76. Found: C, 82.60; H, 5.33; N, 8.71. IR (cm^{-1}): 3063w, 1604w, 1575w, 1538s *ν*(C═C; C═N). ^1H NMR ($CDCl_3$, 298 K): *δ*, 1.71 (s, 3H, C3−CH_3), 6.89 (d, 2H), 7.14−7.64 (m, 4H), 7.83 (d, 1H), 8.10 (d, 2H), 8.29 (d, 1H), 13.40 (sbr, 1H, −NH). ^{13}C NMR ($CDCl_3$, 298 K): *δ*, 16.5 (s, C3−CH_3), 102.0 (s, *C*4), 119.6, 122.4, 124.1, 124.8, 125.1, 126.9, 127.1, 127.4, 127.6, 128.3, 128.6, 129.0, 129.1, 129.5, 130.4, 133.5, 134.1, 139.1, 139.6, 143.1, 148.3, 164.2, 166.4 (s, ligand $HL^{biph,naph}$). ESI-MS (−) CH_3OH (*m*/*z*, relative intensity %): 478 [100] $[L^{biph,naph}]^-$.

Ligand $HL^{ph,naph}$. The synthesis was performed as for $HL^{biph,ph}$ using 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (1.57 g, 5.64 mmol) and 1-naphthylamine (0.80 g, 5.64 mmol). The compound is soluble in

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diethyl ether, alcohols, acetone, acetonitrile, DMSO, and chlorinated solvents. Mp: 175−176 °C. Anal. Calcd for $C_{27}H_{21}N_3O$: C, 80.34; H, 5.25; N, 10.42. Found: C, 80.48; H, 5.32; N, 10.41. IR (cm^{-1}): 3043w, 1615s, 1587s, 1571s, 1532m, 1514w, 1503w ν(C═C; C═N). ^{1}H NMR ($CDCl_3$, 298 K): δ, 1.60 (s, 3H, C3−CH_3), 6.84 (d, 1H), 7.11−7.63 (m, 12H), 7.82 (d, 1H), 8.08 (d, 2H), 8.26 (d, 1H), 13.31 (sbr, 1H, −NH). ^{13}C NMR ($CDCl_3$, 298 K): δ, 16.3 (s, C3−CH_3), 101.9 (s, *C*4), 119.6, 122.3, 124.0, 124.7, 125.0, 126.9, 127.4, 127.5, 128.4, 128.5, 128.6, 129.0, 129.5, 130.4, 131.6, 133.4, 134.1, 139.1, 148.3, 164.4, 166.3 (s, ligand $HL^{ph,naph}$). ESI-MS (−) CH_3OH (*m*/*z*, relative intensity %): 402 [100] $[L^{ph,naph}]^-$.

Ligand $HL^{hex,naph}$. The synthesis was performed as for $HL^{biph,ph}$ using 1-phenyl-3-methyl-4-hexenyl-5-pyrazolone (1.61 g, 5.64 mmol) and 1-naphthylamine (0.80 g, 5.64 mmol). The compound is soluble in diethyl ether, alcohols, acetone, acetonitrile, DMSO, and chlorinated solvents. Mp: 166−168 °C. Anal. Calcd for $C_{27}H_{29}N_3O$: C, 78.80; H, 7.10; N, 10.21. Found: C, 78.86; H, 7.26; N, 10.16. IR (cm^{-1}): 3058w, 1623s, 1585s, 1572s, 1538s ν(C═C; C═N). ^{1}H NMR (CDCl3, 298 K): δ, 0.71 (t, 3H, $CH_2CH_2CH_2(CH_2)_2CH_3$), 0.94−1.06 (m, 4H, $CH_2CH_2CH_2(CH_2)_2CH_3$), 1.12 (m, 2H, $CH_2CH_2CH_2(CH_2)_2CH_3$), 1.47 (m, 2H, $CH_2CH_2CH_2(CH_2)_2CH_3$), 2.47 (s, 3H, C3−CH_3), 2.57 (m, 2H, $CH_2CH_2CH_2(CH_2)_2CH_3$), 7.16−7.97 (m, 10H), 8.05 (d, 2H), 13.29 (sbr, 1H, −NH). ^{13}C NMR ($CDCl_3$, 298 K): δ, 14.0 (s, $(CH_2)_6CH_3$), 17.2 (s, C3−CH3), 22.3, 29.2, 29.5, 29.6, 31.0 (s, $(CH_2)_6CH_3$), 99.8 (s, *C*4), 119.5, 122.7, 124.6, 125.3, 127.2, 127.8, 128.6, 129.0, 130.3, 133.1, 133.2, 134.5, 139.3, 147.1, 166.6, 169.8 (s, ligand). ESI-MS (−) CH_3OH (*m*/*z*, relative intensity %): 410 [100] $[L^{hex,naph}]^-$.

[Ru(cym)($L^{biph,ph}$*)Cl] (**1**).* To the proligand $HL^{biph,ph}$ (280.0 mg, 0.652 mmol) dissolved in methanol (20 mL) was added KOH (36.5 mg, 0.652 mmol). The mixture was stirred for 1 h at room temperature, and then $[Ru(cym)Cl_2]_2$ (200.0 mg, 0.326 mmol) was added. The resulting solution was stirred under reflux for 24 h. The solvent was removed under reduced pressure, dichloromethane (10 mL) was added, and the mixture was filtered to remove potassium chloride. The solution was concentrated to ca. 2 mL and stored at 4 °C, affording red crystals (360.0 mg, 0.514 mmol, yield 79%) that are soluble in diethyl ether, alcohols, acetone, acetonitrile, DMSO, and chlorinated solvents. Mp: 247−249 °C. Anal. Calcd for $C_{39}H_{36}N_3RuClO$: C, 66.99; H, 5.19; N, 6.01. Found: C, 67.00; H, 5.02; N, 5.94. Λ_m (DMSO, 298 K, 10^{-4} mol/L): 18 S cm^2 mol^{-1}. Λ_m (DMSO, 313 K, 10^{-4} mol/L): 40 S cm^2 mol^{-1}. Λ_m (DMSO, 333 K, 10^{-4} mol/L): 61 S cm^2 mol^{-1}. Λ_m (DMSO, 353 K, 10^{-4} mol/L): 74 S cm^2 mol^{-1}. IR (cm^{-1}): 3034w, 1599m, 1588s, 1572s, 1530w ν(C═C; C═N). ^{1}H NMR ($CDCl_3$, 298 K): δ, 1.24 (d, 3H, ^3J = 6.8 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 1.28 (s, 3H, C3−CH_3), 1.31 (d, 6H, ^3J = 6.8 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 2.06 (s, 3H, CH_3-C_6H_4−$CH(CH_3)_2$), 2.74 (sept, 1H, ^3J = 7.2 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 3.52 (d, 1H, ^3J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 5.14 (d, 1H, ^3J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 5.17 (d, 1H, ^3J = 6.4 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 5.37 (d, 1H, ^3J = 6.4 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 6.82−7.96 (m, 19H). ^{13}C NMR ($CDCl_3$, 298 K): δ, 15.7 (s, C3−CH_3), 18.7 (s, CH_3−C_6H_4−$CH(CH_3)_2$), 21.2 and 23.8 (s, CH_3−C_6H_4−$CH(CH_3)_2$), 30.9 (s, CH_3−C_6H_4−$CH(CH_3)_2$), 79.2, 80.3, 82.5, 83.7, 84.3, 86.9 (s, CH_3−C_6H_4−$CH(CH_3)_2$), 102.4 (s, *C*4), 120.6, 124.7, 124.9, 125.2, 125.9, 126.8, 127.1, 127.3, 127.4, 128.7, 128.9, 129.0, 129.5, 135.0, 139.6, 140.2, 140.6, 149.4, 156.2, 160.4, 168.3 (s, ligand $H^{biph,ph}$). ESI-MS (+) CH_3OH (*m*/*z*, relative intensity%): 664 [100][Ru(cym)-$(L^{biph,ph})]^+$.

[Ru(benz)($L^{biph,ph}$*)Cl] (**2**).* The synthesis was performed as for **1** using $[Ru(benz)Cl_2]_2$. **2** is soluble in alcohols, acetone, acetonitrile, DMSO, and chlorinated solvents. Mp: 240−242 °C. Anal. Calcd for $C_{35}H_{28}N_3RuClO$: C, 65.36; H, 4.39; N, 6.53. Found: C, 65.16; H,4.43; N, 6.31. Λ_m (DMSO, 298 K, 10^{-4} mol/L): 16 S cm^2 mol^{-1}. IR (cm^{-1}): 3066w, 1590s, 1568s, 1526m ν(C═C; C═N). ^{1}H NMR ($CDCl_3$, 298 K): δ, 1.27 (s, 3H, C3−CH_3), 5.21 (s, 6H, C_6H_5), 6.89−7.95 (m, 19H). ^{13}C NMR ($CDCl_3$, 298 K): δ, 15.6 (s, C3−CH_3), 84.6s (s, C_6H_6), 102.8 (s, *C*4), 102.4 (s, *C*4), 119.5, 120.8, 124.8, 124.9, 125.3, 125.8, 126.8, 127.0, 127.3, 127.5, 128.5, 128.5 129.3, 129.2, 134.8, 139.4, 140.1, 140.7, 143.4, 149.5, 156.6, 160.6, 168.5 (s, ligand $H^{biph,ph}$). ESI-MS (+) CH_3OH (*m*/*z*, relative intensity %): 608 [100][Ru(benz)$(L^{biph,ph})]^+$.

[Ru(hmb)($L^{biph,ph}$*)Cl] (**3**).* The synthesis was performed as for **1** using $[Ru(hmb)Cl_2]_2$. **3** is soluble in alcohols, acetone, acetonitrile, DMSO, and chlorinated solvents. Mp: 248−250 °C. Anal. Calcd for $C_{41}H_{40}N_3RuClO$: C, 67.71; H, 5.54; N, 5.78. Found: C, 67.27; H, 5.46; N, 5.59. Λ_m (DMSO, 298 K, 10^{-4} mol/L): 18 S cm^2 mol^{-1}. IR (cm^{-1}): 3056w, 1601w, 1587m, 1567s, 1527m ν(C═C; C═N). ^{1}H NMR ($CDCl_3$, 298 K): δ, 1.23 (s, 3H, C3−CH_3), 1.78 (s, 18H, $C_6(CH_3)_6$), 6.73−7.94 (m, 19H). ^{13}C NMR ($CDCl_3$, 298 K): δ, 15.2 (s, C3−CH_3), 16.1 (s, $C_6(CH_3)_6$), 92.0 (s, $C_6(CH_3)_6$), 102.8 (s, *C*4), 119.5, 120.9, 121.8, 124.0, 124.9, 125.0, 126.7, 127.1, 127.7, 128.4, 128.6, 128.9, 129.6, 136.1, 139.4, 140.1, 140.3, 149.5, 154.5, 160.3, 169.4 (s, ligand $H^{biph,ph}$). ESI-MS (+) CH_3OH (*m*/*z*, relative intensity %): 692 [100][Ru(hmb)Ru$(L^{biph,ph})]^+$.

[Ru(cym)($L^{biph,naph}$*)Cl] (**4**).* The synthesis was performed as for **1** using $HL^{biph,naph}$. **4** is soluble in alcohols, acetone, acetonitrile, DMSO, and chlorinated solvents. Mp: 248−249 °C. Anal. Calcd for $C_{43}H_{38}N_3RuClO$: C, 68.93; H, 5.11; N, 5.61. Found: C, 68.79; H, 5.01; N, 5.50. Λ_m (DMSO, 298 K, 10^{-4} mol/L): 17 S cm^2 mol^{-1}. IR (cm^{-1}): 3041w, 1589m, 1570s, 1509m ν(C═C; C═N).). ^{1}H NMR ($CDCl_3$, 298 K): δ, 1.18 (d, 6H, C3−CH_3), 1.24 and 1.34 (m, 12H, CH_3−C_6H_4−$CH(CH_3)_2$), 1.90 (s, 6H, CH_3-C_6H_4−$CH(CH_3)_2$), 2.75 (m, 2H, CH_3−C_6H_4−$CH(CH_3)_2$), 2.94 (d, 1H, ^{3}J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 3.27(d, 1H, ^{3}J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 4.71 (d, 1H, ^{3}J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 4.91 (d, 1H, ^{3}J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 4.97 (d, 1H, ^{3}J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 5.10 (d, 1H, ^{3}J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 5.30 (d, 1H, ^{3}J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 5.38 (d, 1H, ^{3}J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 6.90−8.20 (m, 20H), 9.11 (d,2H). ^{13}C NMR ($CDCl_3$, 298 K): δ, 15.7, 15.8 (s, C3−CH_3), 18.7, 18.9 (s, CH_3−C_6H_4−$CH(CH_3)_2$), 21.2, 21.4 and 23.8, 23.9 (s, CH_3−C_6H_4−$CH(CH_3)_2$), 30.8, 30.9 (s, CH_3−C_6H_4−$CH(CH_3)_2$), 80.2, 80.3, 83.7, 83.8, 84.3, 84.5, 87.0,87.2, 96.5, 96.7, 101.2, 101.4 (s, CH_3−C_6H_4−$CH(CH_3)_2$), 102.4, 102.6 (s, *C*4), 120.6, 121.0, 124.7,124.8, 124.9, 152.1, 125.2, 125.9, 126.1, 126.6, 126.8, 127.1, 127.3, 127.4, 128.2, 128.7, 128.9 129.0, 129.5, 135.0, 135.4, 139.6, 139.9, 140.2, 140.5, 140.6, 149.2, 149.4, 156.0, 156.2, 159.9, 160.4, 168.3, 168.6 (s, ligand $H^{biph,naph}$). ESI-MS (+) CH_3OH (*m*/*z*, relative intensity %): 714 [100][Ru(cym)$(L^{biph,naph})]^+$.

[Ru(cym)($L^{ph,naph}$*)Cl] (**5**).* The synthesis was performed as for **1** using $HL^{ph,naph}$. **5** is soluble in alcohols, acetone, acetonitrile, DMSO, and chlorinated solvents. Mp: 213-215 °C. Anal. Calcd for $C_{37}H_{34}N_3RuClO$: C, 66.01; H, 5.09; N, 6.24. Found: C, 65.86; H, 5.00; N, 6.20. Λ_m (DMSO, 298 K, 10^{-4} mol/L): 15 S cm^2 mol^{-1}. IR (cm^{-1}): 3033m, 1587m, 1567s, 1527m ν(C═C; C═N). ^{1}H NMR ($CDCl_3$, 298 K): δ, 1.12−1.30 (d, 12H, CH_3−C_6H_4−$CH(CH_3)_2$ ^{3}J = 7.2 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 1.19−1.34 (d, 6H, CH_3−C_6H_4−$CH(CH_3)_2$ ^{3}J = 6.8 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 1.66 (s, 3H, C3−CH_3), 1.80 (s, 6H, C3−CH3), 2.08 (s, 3H, CH_3−C_6H_4−$CH(CH_3)_2$), 2.11 (s, 6H, CH_3−C_6H_4−$CH(CH_3)_2$), 2.75 (m, 3H, CH_3−C_6H_4−$CH(CH_3)_2$), 2.90 (d, 1H, ^{3}J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 3.23 (d, 2H, ^{3}J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 4.67 (d, 1H, ^{3}J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 4.88 (d, 2H, ^{3}J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 4.93 (d, 2H, ^{3}J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 5.07 (d, 1H, ^{3}J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 5.26 (d, 1H, ^{3}J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 5.34 (d, 1H, ^{3}J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 6.73−9.04 (m, 51H). ^{13}C NMR ($CDCl_3$, 298 K): δ, 15.5, 15.7 (s, C3−CH_3), 18.7, 18.8 (s, CH_3−C_6H_4−$CH(CH_3)_2$), 21.4, 21.5 and 23.4, 23.6 (s, CH_3−C_6H_4−$CH(CH_3)_2$), 31.0, 31.2 (s, CH_3−C_6H_4−$CH(CH_3)_2$), 80.0, 80.1, 83.9, 84.4, 84.6, 84.9, 87.0, 87.2, 96.5, 96.7, 101.0, 101.2 (s, CH_3−C_6H_4−$CH(CH_3)_2$), 102.2, 103.3 (s, *C*4), 120.4, 121.2, 124.7, 124.7, 124.9, 152.0, 125.6, 125.9, 126.3, 126.5, 126.8, 127.1, 127.3, 127.6, 128.6, 128.7, 129.0, 129.5, 135.0, 135.4, 139.6, 139.9, 140.2, 140.5, 140.6, 149.2, 149.4, 156.0, 156.2, 160.7, 161.4, 170.2, 170.6 (s, ligand $H^{ph,naph}$). ESI-MS (+) CH_3OH (*m*/*z*, relative intensity %): 638 [100][Ru(cym)Ru$(L^{ph,naph})]^+$.

[Ru(benz)($L^{ph,naph}$*)Cl] (**6**).* The synthesis was performed as for **2** using $HL^{ph,naph}$. **6** is soluble in alcohols, acetone, acetonitrile, DMSO, and chlorinated solvents. Mp: 298−300 °C. Anal. Calcd for

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$C_{33}H_{26}N_3RuClO$: C, 64.23; H, 4.25; N, 6.81. Found: C, 64.06; H, 4.20; N, 6.71. Λ_m (DMSO, 298 K, 10^{-4} mol/L): 18 S cm^2 mol^{-1}. IR (cm^{-1}): 3070w, 1585m, 1566s, 1523m, 1505w ν(C═C; C═N). ^{1}H NMR ($CDCl_3$, 298 K): δ, 1.13 (s, 6H, C3−CH_3), 1.15 (s, 3H, C3−CH3), 4.94 (s, 6H, C_6H_6), 5.03 (s, 12H, C_6H_6), 6.80−9.12 (m, 51H). ^{13}C NMR ($CDCl_3$, 298 K): δ, 15.1, 15.2 (s, C3−CH_3), 84.3, 84.5 (s, C_6H_6), 103.2, 105.1 (s, *C*4), 119.5, 120.6, 120.7, 122.8, 123.7, 124.0, 124.6, 124.9, 125.4, 125.9, 126.1, 126.3, 126.4, 126.8, 126.9, 127.5, 127.6, 127.7, 127.9, 128.2, 128.5, 128.7, 129.3, 129.9, 133.3, 133.6, 135.3, 136.1, 139.3, 143.2, 149.4, 149.5, 152.7, 153.1, 161.2, 162.4, 168.9, 170.3 (s, ligand $L^{ph,ph}$). ESI-MS (+) CH_3OH (*m*/*z*, relative intensity %): 582 [100][Ru(benz)($L^{ph,naph}$)]$^+$.

[Ru(hmb)($L^{ph,naph}$)Cl] (**7**). The synthesis was performed as for **3** using $HL^{ph,naph}$. **7** is soluble in alcohols, acetone, acetonitrile, DMSO, and chlorinated solvents. Mp: 248−250 °C. Anal. Calcd for $C_{39}H_{38}N_3RuClO$: C, 66.80; H, 5.46; N, 5.99. Found: C, 66.57; H, 5.34; N, 5.78. Λ_m (DMSO, 298 K, 10^{-4} mol/L): 20 S cm^2 mol^{-1}. IR (cm^{-1}): 3055w, 1600w, 1584m, 1563s, 1525m ν(C═C; C═N). ^{1}H NMR ($CDCl_3$, 298 K): δ, 1.04 (s, 3H, C3−CH_3), 1.06 (s, 6H, C3−CH_3), 1.54 (s, 6H, $C_6(CH_3)_6$), 1.60 (s, 12H, $C_6(CH_3)_6$), 6.57−7.94 (m, 45H), 8.01 (d, 4H) 8.01 (d, 2H). ^{13}C NMR ($CDCl_3$, 298 K): δ, 15.2, 15.4 (s, C3−CH_3), 16.1, 16.2 (s, $C_6(CH_3)_6$), 92.0, 93.4 (s, $C_6(CH_3)_6$), 102.8, 103.0 (s, *C*4), 119.5, 120.2, 120.9, 121.8, 124.0, 124.9, 125.1, 125.6, 125.8, 126.2, 126.6, 126.9, 127.1, 127.5, 127.7, 127.9, 128.1, 128.4, 128.6, 128.9, 129.3, 129.6, 136.1, 136.6, 139.4, 140.1, 140.3, 149.2 149.5, 153.6, 154.5, 160.3, 161.7, 169.4, 170.0 (s, ligand $H^{ph,naph}$). ESI-MS (+) CH_3OH (*m*/*z*, relative intensity %): 666 [100][Ru(hmb)Ru($L^{ph,naph}$)]$^+$.

[Ru(cym)($L^{hex,naph}$)Cl] (**8**). The synthesis was performed as for **1** using $HL^{hex,naph}$. **8** is soluble in alcohols, acetone, acetonitrile, DMSO, and chlorinated solvents. Mp: 200−202 °C. Anal. Calcd for $C_{37}H_{42}N_3RuClO$: C, 65.23; H, 6.21; N, 6.17. Found: C, 65.20; H, 6.29; N, 6.13. Λ_m (DMSO, 298 K, 10^{-4} mol/L): 17 S cm^2 mol^{-1}. IR (cm^{-1}): 3052w, 1590s, 1573s, 1520m ν(C═C; C═N). ^{1}H NMR ($CDCl_3$, 298 K): δ, 0.68 (m, 3H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 0.89 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.01 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.10, 1.21 (d, 3H, ^{3}J = 7.2 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 1.16, 1.31 (d, 3H, ^{3}J = 6.8 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 1.42 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 1.55, 1.59 (s, 3H, CH_3-C_6H_4−$CH(CH_3)_2$), 1.94 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.33, 2.24 (s, 3H, C3−CH_3), 2.42 (m, 2H, $CH_2CH_2CH_2CH_2CH_2CH_3$), 2.63 (m, 1H, CH_3−C_6H_4−$CH(CH_3)_2$), 2.95 (d, 1H, ^{3}J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 3.09 (d, 1H, ^{3}J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 4.75 (d, 1H, ^{3}J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 4.86 (d, 1H, ^{3}J = 5.6 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 4.89 (d, 1H, ^{3}J = 6.4 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 4.92 (d, 1H, ^{3}J = 6.4 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 5.23 (d, 1H, ^{3}J = 6.4 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 5.33 (d, 1H, ^{3}J = 6.4 Hz, CH_3−C_6H_4−$CH(CH_3)_2$), 7.15−8.79 (12, H). ^{13}C NMR ($CDCl_3$, 298 K): δ, 14.0 (s, −$(CH_2)_5CH_3$), 17.2, 17.6 (s, CH_3−C_6H_4−$CH(CH_3)_2$), 18.0 (s, C3−CH_3), 20.8 and 23.8, 23.0.9, and 23.7 (s, CH_3−C_6H_4−$CH(CH_3)_2$), 22.3 (s, −$CH_2(CH_2)_4CH_3$), 29.3, 29.4, 29.9, 30.6, 30.7, 30.8, 31.8. 31.1, 32.4, 32.9 (s, CH_3−C_6H_4−$CH(CH_3)_2$ and −$(CH_2)_5CH_3$), 76.2, 80.0, 82.6, 83.5, 84.6, 84.7, 87.8, 92.9, 93.5, 101.1 (s, CH_3−C_6H_4−$CH(CH_3)_2$), 102.9, 103.3 (s, *C*4), 119.6, 120.3, 120.9, 122.1, 123.5, 124.6, 124.7, 126.0, 126.2, 126.7, 127.2, 127.4, 127.9, 128.1, 128.5, 128.9, 129.1, 129.4, 131.2, 133.8, 134.3, 139.6, 147.5, 147.6, 151.9, 152.9, 161.0, 171.2, 172.9 (s, ligand $H^{hex,naph}$). ESI-MS (+) CH_3OH (*m*/*z*, relative intensity %): 646 [100][Ru(cym)-($L^{hex,naph}$)]$^+$.

[Ru(hmb)($L^{hex,naph}$)Cl] (**9**). The synthesis was performed as for **3** using $HL^{hex,naph}$. **9** is soluble in alcohols, acetone, acetonitrile, DMSO, and chlorinated solvents. Mp: 250−252 °C. Anal. Calcd for $C_{39}H_{46}N_3RuClO$: C, 66.04; H, 6.54; N, 5.92. Found: C, 65.97; H, 6.46; N, 5.79. Λ_m (DMSO, 298 K, 10^{-4} mol/L): 15 S cm^2 mol^{-1}. IR (cm^{-1}): 3056w, 1601w, 1587m, 1567s, 1527m ν(C═C; C═N).). ^{1}H NMR ($CDCl_3$, 298 K): δ, 0.66 (s, 3H, −$(CH_2)_5CH_3$), 0.80−1.04 (m, 6H, −$(CH_2)_5CH_3$), 1.45 (m, 2H, −$(CH_2)_5CH_3$), 1.53 (s, 3H, C3−CH_3), 1.55 (s, 18H, $C_6(CH_3)_6$), 2.30 (m, 2H, −$(CH_2)_5CH_3$), 7.13−8.27 (m, 12H). ^{13}C NMR ($CDCl_3$, 298 K): δ, 14.0 (s, −$(CH_2)_5CH_3$), 15.4 (s, $C_6(CH_3)_6$), 17.9 (s, C3−CH_3), 22.3 (s, −$CH_2(CH_2)_4CH_3$), 29.0, 29.4, 31.0, 31.7, 33.0 (s, −$(CH_2)_5CH_3$), 91.6 (s, $C_6(CH_3)_6$), 101.2 (s, *C*4), 119.5, 121.1, 122.5, 122.7, 123.5, 124.0, 124.6, 124.8, 125.4, 126.6, 127.2, 127.7, 128.3, 128.6, 128.8, 128.9, 129.1, 130.2, 133.9, 139.4, 147.4, 151.4, 160.9, 169.7, 175.2 (s, ligand $H^{hex,naph}$). ESI-MS (+) CH_3OH (*m*/*z*, relative intensity %): 674 [100][Ru(hmb)-($L^{hex,naph}$)]$^+$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table of crystal data and details of the structure determination. Crystallographic data in CIF format. 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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