



Luminescent Ru Complexes

Luminescent Carbonyl Hydrido Ruthenium(II) Diimine Coordination Compounds: Structural, Photophysical, and Electrochemical Properties

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Abstract: A series of luminescent carbonyl hydrido ruthenium-(II) complexes with various diimine ligands with diverse electronic properties, including Me₂bpy (bpy = bipyridine), Me₂phen (phen = phenanthroline), PhenCOOH, PhenCN, Me₂Ph₂phen, Ph₂phen, and π -conjugating dipyrido[3,2-*d*:2',3'-*f*]quinoxaline (dpq), dipyrido[3,2-*a*:2',3'-*c*](6,7,8,9-tetrahydro)phenazine (dpqc), and dipyridophenazine (dppz) have been synthesized and characterized. Four of these complexes have

been structurally characterized by X-ray crystallography. The photophysical and electrochemical properties of these complexes have been studied. The effects of the electronic features and π -conjugation of the diimine ligand on the electronic and photophysical properties of these complexes have also been discussed. Our study revealed that the luminescence performance of these complexes could be significantly enhanced by increasing the rigidity and π -conjugation of the diimine ligand.

Introduction

Tris(bipyridyl) Rull complex and its derivatives have been extensively studied, owing to the rich photophysical properties including their metal-to-ligand charge-transfer (MLCT) phosphorescent, as well as good thermal and photostability.^[1-3] These complexes have been used in a wide variety of applications including photosensitizers, photochemical molecular devices, dye-sensitized solar cells as well as biological applications such as DNA probes, lipid probes, and fluorescence-polarization immunoassays.^[4-11] The ease of the modification of the redox properties as well as the ground-state and excited-state properties of this family of complexes through the functionalization of the bipyridine ligands is also an attractive feature of this class of complexes.^[12-17] Previous studies have revealed that the replacement of one of the diimine ligands in $[Ru^{II}(bpy)_3]^{2+}$ (bpy = bipyridine) with phosphine ligands can significantly increase the guantum yields of the complexes.^[18] The decrease in molecular symmetry by replacing one or two of the diimine ligands

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On the basis of our recent work on luminescent carbonyl hydridoquinolinolato Ru^{II} complexes,^[23] we report here a new series of luminescent carbonyl hydrido Ru^{II} diimine complexes bearing different types of diimine ligands such as Me₂bpy, Me₂phen (phen = phenanthroline), PhenCOOH, PhenCN, Me₂Ph₂phen, Ph₂phen, and π -conjugating dipyrido[3,2-d:2',3'-f]-quinoxaline (dpq), dipyrido[3,2-a:2',3'-c](6,7,8,9-tetrahydro)-phenazine (dpqc), and dipyridophenazine (dppz). The photophysical and electrochemical properties of these complexes have been investigated. The effects of the electronic and steric properties of the diimine ligands on the luminescent properties of the complexes will be discussed.

Results and Discussion

Synthesis and Characterization

The diimine ligands 1,10-phenanthroline-2-carboxylic acid (PhenCOOH),^[24] 2-cyano-1,10-phenanthroline (PhenCN),^[24] dipyrido[3,2-d:2',3'-f]quinoxaline (dpq),^[25] dipyrido[3,2-a:2',3'-c](6,7,8,9-tetrahydro)phenazine (dpqc),^[25] and dipyridophenazine (dppz)^[26] were prepared according to literature procedures. The luminescent carbonyl hydrido ruthenium(II) diimine complexes [Ru^{II}(N N)(CO)(H)(PPh₃)₂]PF₆ [N N = Me₂bpy (1), Me₂phen (2), PhenCOOH (3), Me₂Ph₂phen (5), Ph₂phen (6), dpq (7), dpqc (8), dppz (9)] were prepared by ligand-substitution





reactions of the carbonyl bis(hydrido)tris(triphenylphosphine)ruthenium(II) precursor [Ru^{II}(CO)(H)₂(PPh₃)₃] with the corresponding diimine ligands in ethanol under reflux conditions (Scheme 1). Attempts were also made to use [Ru^{II}(CO)(H)Cl-(PPh₃)₃] as the synthetic precursor; however, a mixture of $[Ru^{II}(N N)(CO)(H)(PPh_3)_2]^+$ and $[Ru^{II}(N N)(CO)(CI)(PPh_3)_2]^+$ were formed in this case, which are difficult to separate owing to their similar solubility and polarity. Similar reaction between $[Ru^{II}(CO)(H)_{2}(PPh_{3})_{3}]$ and PhenCN leads to the formation of $[Ru^{II}(PhenCONH_2)(CO)(PPh_3)_2]^+$ instead of the expected complex $[Ru^{II}(PhenCN)(CO)(H)(PPh_3)_2]^+$, owing to the hydrolysis of the coordinated ligand PhenCN. Electrospray ionization mass spectrometry (ESI-MS) of the amide complex shows a predominant peak at m/z = 876 in the positive range, corresponding to the parent ion peak. There is also a strong C=O stretch at 1622 cm⁻¹ and a sharp N-H stretch at 3163 cm⁻¹ in the IR spectrum. Hydrolysis of the PhenCN ligand could be prevented by carrying out the reaction in the presence of Et₂NH·HCl. In this way, trans-[Ru^{II}(PhenCN)(CO)(H)(PPh₃)₂]⁺ is obtained as the PF_6^{-1} salt in excellent yield. All the complexes have been characterized by ¹H NMR, ³¹P{¹H} NMR, IR spectroscopy, ESI-MS, and elemental analysis. The structures of 3 and 7-9 have been determined by X-ray crystallography.



Scheme 1. Synthetic routes to 1-9.

Complexes 1–9 all exhibit a predominant [*M*]⁺ peak in the ESI-MS (*m*/*z* = 839 for 1, *m*/*z* = 863 for 2, *m*/*z* = 879 for 3, *m*/*z* = 860 for 4, *m*/*z* = 1015 for 5, *m*/*z* = 987 for 6, *m*/*z* = 887 for 7, *m*/*z* = 941 for 8, and *m*/*z* = 937 for 9). In the IR spectra, except 4 and 6, the complexes all show one weak and one strong absorption in the region 1906–2030 cm⁻¹, corresponding to ν (Ru–H) and ν (C=O) stretches, respectively. These ν (Ru–H) and ν (C=O) stretching frequencies are comparable to those in [Ru^{II}(CO)(H)₂(PPh₃)₃] and are in the typical range reported for related complexes.^[27] The different π -accepting properties of these diimine ligands are reflected in the stretching frequencies of the C=O stretches of these complexes. The ν (Ru–H) stretch is not observed for 4 and 6 probably owing to overlap of the ν (Ru–H) band with the strong and relatively broad ν (C=O) absorption. The counter anions (PF₆⁻) of these complexes are char-

acterized by the strong ν (P–F) stretches at around 840 cm⁻¹. The carboxylic acid and cyano substituents in the diimine ligands of **3** and **4** are characterized by ν (C=O) at 1618 cm⁻¹ and ν (C=N) at 2237 cm⁻¹.

All complexes show ¹H NMR and ³¹P{¹H} NMR signals with chemical shifts and integral ratios consistent with their proposed structures. The hydrido ligands in these complexes are characterized by the upfield triplet signals with chemical shift (δ) in the range -9.61 to -12.09 ppm in the ¹H NMR spectra. The triplet splitting of the hydride signals with coupling constants of 18.5 to 19.9 Hz is the result of the coupling between the hydrido ligand and the phosphorus atoms of the two chemically equivalent cis-phosphine ligands. The coupling constants are also in the typical range found for related hydrido ruthenium(II) phosphine complexes.^[28] Although the two pyridyl moieties are related by symmetry in the free diimine ligands of 1, 2, 5-7, and 9, the ¹H signals of the two pyridyl moieties in these complexes split into two sets (Figures S1-S5 in the Supporting Information). This suggest that these diimine ligands are trans to two different ligands. In the ³¹P{¹H} NMR spectra, the two PPh₃ in each of these complexes only show a singlet signal with a chemical shift (δ) in the range 44.5-47.4 ppm and the PF_6^- anion is characterized by a septet signal at about δ = -144 ppm. The observation of the sharp singlet signals in the ³¹P{¹H} NMR spectra together with the unsymmetrical chemical environments for the two pyridyl moieties of the diimine ligands confirms the geometric isomerism of these complexes, in which the diimine ligands are trans to the carbonyl and the hydrido ligand, and the two triphenylphosphine ligands are arranged in a trans configuration. The geometrical arrangements of these ligands are further confirmed by the Xray crystal structures of 3, 7, 8, and 9.

X-ray Crystal Structure Determination

By slow diffusion of diethyl ether into concentrated dichloromethane solutions of the complexes, single crystals of 3 and 7-9 with quality suitable for X-ray crystallography were obtained. The perspective drawings of the complex cations of 3 and 7-9 are shown in Figure 1. The crystal data and selected bond lengths and angles are given in Tables S1 and S2, respectively. In these structures, the ruthenium centers adopt distorted octahedral geometries with two PPh3 ligands trans to each other and located in the axial positions relative to the diimine ligand, which is trans to one carbonyl ligand and one hydrido ligand. The presence of a PF_6^- counter anion in each of these complexes has also been identified. In all these structures, the Ru-C(CO) distances are in the range 1.84–1.87 Å, which are in good agreement with those reported for related Rull complexes.^[29] As found in the crystal structures of other Ru^{II} diimine complexes,^[30] the bite angles of the chelating diimine ligands at the Ru^{II} metal centers are in range 75.9–76.9°. Except for the structure of 3, the Ru–N bond lengths of all of these complexes are in the range 2.120–2.199 Å, typical for Ru^{II} diimine complexes.^[31] The significantly longer Ru–N bond adjacent to the carboxylic acid substituent in 3 (2.236 Å) can be attributed to steric hindrance of the bulky -COOH group on the cis-carbonyl





ligand. The carboxylic acid group in the structure of **3** is close to the carbonyl and is non-coplanar with the phenanthroline plane with a dihedral angle of 53.8° to minimize steric repulsion. Both ¹H NMR and ³¹P NMR spectroscopy confirmed that there is only one geometrical isomer present in solution in all these complexes. In the structures of **7–9**, the diimine ligands showed a good coplanarity even for **8**, with a cyclohexyl moiety, which shows a high degree of disorder on the carbon atom of the cyclohexyl ring.



Figure 1. ORTEP drawings of the cationic structures of (a) **3**, (b) **7**, (c) **8**, and (d) **9**. Hydrogen atoms, except the hydrido ligand and that in the carboxylic acid group, have been omitted for clarity. Thermal ellipsoids are drawn at the 30 % probability level.

The two PPh₃ ligands are slightly bent towards the carbonyl group as revealed from the angles of P-Ru-P being in the range 165.2-170.2°. This is probably due to the steric repulsion between the phenyl rings of the PPh₃ and the chelating diimine ligands. Close scrutiny of the phosphine and the diimine ligands in these crystal structures reveals that there are $\pi \cdots \pi$ interactions between the diimine ligand and phenyl rings of the PPh₃ ligands. These $\pi \cdots \pi$ interactions are characterized by centroid-to-centroid distances of 3.5-3.9 Å between the two interacting rings as illustrated in the structures of complexes 3 and **9** (Figure 2). In addition to intramolecular $\pi \cdots \pi$ interactions between the phosphine and diimine ligands, an intermolecular hydrogen-bonding interaction between the carboxylic acids of adjacent molecules in the structure of 3 also occurs and is characterized by the short O···O distance of 2.78 Å, indicative of an O-H···O interaction (Figure 2).



Figure 2. The supramolecular interactions in the structures of (a) 3 and (b) 9.

UV/Vis Absorption Properties

The UV/Vis absorption properties of all complexes in dichloromethane solution have been investigated. These complexes dissolved in dichloromethane give yellow or orange solutions. The UV/Vis absorption data are collected in Table 1 and selected overlaid absorption spectra are shown in Figure 3. The absorption spectra of complexes show intense absorptions with molar extinction coefficients on the order of 10⁴ dm³ mol⁻¹ cm⁻¹ in the high energy UV region (235-330 nm). These are assigned to the ligand-centered (LC) $\pi \rightarrow \pi^*$ transitions of the PPh₃ and diimine ligands. Owing to the extended π -conjugation of the diimine ligands in 4 and 9, their LC absorptions are much lower in energy. In addition to the intense UV absorption, these complexes show moderately intense absorption bands or shoulders with λ_{abs} in the range 390–465 nm with molar extinction coefficients on the order of 10³ dm³ mol⁻¹ cm⁻¹ and tailing to the visible region down to approximately 470-540 nm. These absorption bands or shoulders are ascribed to the ¹MLCT $[d\pi(Ru) \rightarrow \pi^*(NN)]$ transitions. In accordance with this assign-

Table 1. UV/Vis absorption data for 1-9 in CH₂Cl₂ solution at 298 K.

	Absorption λ_{abs} [nm] (ϵ [dm ³ mol ⁻¹ cm ⁻¹])
1	267 sh (20980), 271 sh (20270), 290 sh (15620), 308 sh (11870), 396 (1470)
2	226 sh (59060), 275 sh (25090), 318 sh (7230), 395 (870)
3	232 (38680), 270 sh (20220), 276 sh (19800), 325 sh (6160), 425 sh (1370)
4	276 (37350), 290 sh (26010), 324 sh (9080), 378 (3640), 465 (1180)
5	225 sh (61930), 248 sh (38270), 292 sh (33060), 330 sh (10270) 402 (2250)
6	225 sh (55410), 289 sh (28950), 322 sh (12290), 401 sh (3690)
7	256 sh (47680), 298 sh (23600), 322 sh (6550), 401 (2500)
8	224 sh (50380), 268 sh (33460), 308 sh (15860), 342 sh (5653), 404 (1780)
9	225 sh (54850), 277 sh (55990), 312 sh (16940), 364 (10170), 412 (2920)



Figure 3. UV/Vis absorption spectra of $1{-}4$ (a) and $5{-}9$ (b) in CH_2CI_2 solution at 298 K.



ment, these lowest absorptions of the complexes show a strong dependence on the electronic nature of the diimine ligands.

Emission Properties

Complexes **2**, **3**, and **5** with bulky groups at the 2,9-positions of phenanthroline and complex **9** with the dppz ligand are nonemissive in solution at room temperature. The non-emissive nature of **2**, **3**, and **5** can be attributed to the steric effects of the substituents, which weaken the Ru–N bond and the corresponding ligand field strength to render a lower-lying ligand field non-radiative deactivating state.^[32] Whereas for **9**, the nonemissive property is due to the presence of the non-luminescent state associated with the phenazine moiety.^[33]

Except for the complexes with the above non-radiative deactivating factors, this complex system generally shows photoluminescence at room temperature as reflected by the vellow to orange-red emissions observed for 1, 4, and 6-8 (Figure 4). Upon photoexcitation, these complexes in dichloromethane solution at room temperature show structureless emission bands with maxima in the range 573-660 nm and lifetimes in the range 0.14-2.25 us (Table 2). With reference to previous spectroscopic studies of other Ru^{II} diimine complexes^[34] and the observed emission energy trend [1 (573 nm) > 8 (581 nm) > 6(584 nm) > 7 (595 nm) > 4 (660 nm)], which is in line with the decreasing π -accepting ability of the diimine ligands, these emissions are assigned to MLCT $[d\pi(Ru) \rightarrow \pi^*(NN)]$ phosphorescence. It is noteworthy that the increase in rigidity of the diimine ligand framework from 2,2'-bipyridine to the π -conjugated diimine ligands in 7-8 led to improved luminescent quantum yields.[35]



Figure 4. Overlaid emission spectra of $1,\,4,\,6,$ and 8 in CH_2Cl_2 at room temperature.

In 77 K EtOH/MeOH (4:1, v/v) glassy medium, these complexes also display strong luminescence (Figure 5, Table 2). Except for **9**, all complexes show structureless emission bands with a similar energy trend but are considerably blueshifted and longer-lived than their solution emissions. These emissions are also tentatively assigned to be derived from the ³MLCT [$d\pi(Ru) \rightarrow \pi^*(NN)$] excited state. The considerably blueshifted emission in the low-temperature glassy medium is due to the rigidochromic effect commonly observed in MLCT emitters.^[36] The sub-microsecond excited-state lifetimes in the glassy medium at 77 K further support the assignment of a triplet excited

Table 2. Emission data of 1–9.			
	Medium (<i>T</i> [K])	Emission $\lambda_{ m em}{}^{[a]}$ [nm] ($ au_{ m o}$ [µs])	$\phi_{ m em}{}^{ m [b]}$ ($ imes$ 10 ³)
1	CH ₂ Cl ₂ (298) glass ^[c] (77)	573 (0.14) 518 (136.5)	1.1
2	CH ₂ Cl ₂ (298) glass ^[c] (77)	_ ^[d] 517 (237.2)	-
3	CH ₂ Cl ₂ (298) glass ^[c] (77)	_ ^[d] 544 (359.3)	-
4	CH ₂ Cl ₂ (298) glass ^[c] (77)	660 (2.22) 594 (168.2)	3.5
5	CH ₂ Cl ₂ (298) glass ^[c] (77)	_ ^[d] 535 (421.5)	-
6	CH ₂ Cl ₂ (298) glass ^[c] (77)	579 (2.25) 540 (563.1)	25.2
7	CH ₂ Cl ₂ (298) glass ^[c] (77)	592 (2.16) 531 (188.3)	16.1
8	CH ₂ Cl ₂ (298) glass ^[c] (77)	580 (1.82) 518 (161.4)	10.2
9	CH ₂ CI ₂ (298) glass ^[c] (77)	538, 583 (14.5)	-

[a] Excitation at 420 nm. Emission maxima are uncorrected values. [b] Luminescence quantum yield with excitation at 436 nm by using $[Ru(bpy)_3Cl_2]$ as a standard or with excitation at 350 nm by using quinine sulfate as a standard. [c] In EtOH/MeOH (4:1, v/v). [d] Non-emissive.

state. Complex **9** displays luminescence with a highly structured emission band with vibrational progression spacing of approximately 1435 cm⁻¹. The significantly different emission characteristics of **9** is suggestive of a different emission origin. The observation of the structured emission bands suggests the assignment of the ³LC excited state of the dppz ligand.



Figure 5. Overlaid emission spectra of 1, 3, 4, 5, and ${\bf 8}$ in glass medium at 77 K.

The emission of these complexes are found to be slightly sensitive to the solvent environment, which is consistent with their MLCT nature. The emission profiles of complexes **6–8** in different solvent media, such as acetone, MeCN, CH_2Cl_2 , DMF, and MeOH, were investigated and are shown in Figures S6–S8. The emissions of **6** show a blueshift in emission energy with decreasing solvent polarity from a DMF solution (588 nm) to a CH_2Cl_2 solution (582 nm). Such a solvent dependence may be due to the increase in the dipole moment of the excited state, which is more stabilized in a polar solvent medium, in comparison to its ground state. However, complexes **7** and **8** have dpq and dpqc ligands that readily form hydrogen-bonding interactions with protic solvents. Thus, their solvotochromic effects are





more complicated than that of **6** and result from the simultaneous contribution of solvent polarity and hydrogen-bonding effects.

Electrochemistry

The redox properties of all of the complexes in acetonitrile containing 0.1 $\[mmm] nBu_4\]$ NPF₆ were studied by cyclic voltammetry and the electrochemical data are summarized in Table 3. Representative cyclic voltammograms of these complexes are shown in Figure 6. These complexes show an irreversible oxidation wave with E_{pa} in the range +0.74 V to +1.27 V versus Cp₂Fe^{+/0}, which is assigned to metal-centered Ru^{3+/2+} oxidation commonly observed in Ru^{II} diimine complexes.^[37] Such an assignment is supported by the higher oxidation potential observed for complexes with electron-withdrawing substituents and π -conjugating diimine ligands. In the reduction scan, these complexes all show a quasi-reversible reduction couple in the range -1.42 to -2.01 V ($\Delta E_p \approx 61$ -72 mV and $i_{pc}/i_{pa} \approx 0.99$ -1.10 vs. Cp₂Fe^{+/0}). The high sensitivity of the reduction potential to the electronic nature of the diimine ligand is suggestive of the reduction of

Table 3. Electrochemical data for complexes ${\rm 1-9}$ with 0.1 $\rm M~[\it nBu_4N]PF_6$ in MeCN at 298 K. $^{\rm [a]}$

	Oxidation E_{pa} (vs. Fc ^{+/0}) [V] ^[b]	Reduction $E_{1/2}$ (vs. Fc ^{+/0}) [V] ^[b] (ΔE_p [mV]) ^[c]
1	+0.74	-2.01 (68)
2	+0.91	-1.99 (69)
3	+1.22	-1.72 (72)
4	+1.27	-1.52 (85)
5	+0.90	-1.94 (69)
6	+0.85	-1.85 (70)
7	+0.82	-1.78 (70)
8	+0.81	-1.85 (69)
9	+0.80	-1.42 (61), -2.15 (94)

[a] Working electrode: glassy carbon; scan rate: 100 mV s⁻¹. [b] $E_{1/2} = (E_{pa} + E_{pc})/2$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively. [c] $\Delta E_{p} = |E_{pa} - E_{pc}|$.



Figure 6. Cyclic voltammograms of (a) **1** and (b) **9** in 0.1 \bowtie [*n*Bu₄N]PF₆ MeCN solution with scan rate = 100 mV s⁻¹.



the diimine ligand. For **9**, a second quasi-reversible reduction couple at -2.15 V ($\Delta E_p = 94$ mV and $i_{pc}/i_{pa} = 1.14$ vs. Cp₂Fe^{+/0}) is observed, which is assigned to the dppz ligand-based reduction as two successive dppz-based reductions are common for complexes with the dppz ligand.^[38]

Conclusions

We have developed and studied a series of new luminescent Ru^{II} diimine complexes. Except those with non-radiative deactivating diimine ligands, these complexes exhibit MLCT phosphorescence with emission energies, lifetimes, and quantum yields that show strong dependence on the nature of the diimine ligand. Although the quantum efficiencies of these complexes are lower than those of the tris(bipyridyl) Ru^{II} complexes, we demonstrate the possibility of developing new families of luminophores based on Ru^{II} complexes with one diimine ligand and four different other ancillary ligands. We believe that by varying the ancillary ligands we can modify and improve the phosphorescence characteristics. On the basis of these results, further modification of the complexes with various types of ancillary ligands for the development of new luminescent building blocks, photosensitizers, and phosphorescent materials with enhanced luminescence properties is now in progress.

Experimental Section

Materials and Reagents: The diimine ligands, 2,9-dimethyl-1,10phenanthroline (Me₂Phen), 4,4'-dimethyl-2,2'-bipyridine (Me₂bpy), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Me₂Ph₂phen), and 4,7-diphenyl-1,10-phenanthroline (Ph₂Phen) were purchased from Acros Organics. Triphenylphosphine and RuCl₃ were purchased from Strem Chemical Company. These commercially available reagents were used without further purification. The diimine ligands PhenCOOH,^[24] PhenCN,^[24] dpq,^[25] dpqc,^[25] and dppz,^[26] and the precursor complex [Ru^{II}(PPh₃)(CO)(H)₂]^[39] were synthesized according to literature procedures. All other reagents and solvents were of analytical grade and were used without further purification.

Synthesis

General: All reactions were carried out under strictly anaerobic conditions in an inert argon atmosphere by using standard Schlenk techniques.

 $[Ru^{II}(Me_2bpy)(CO)(H)(PPh_3)_2]PF_6$ (1): Me₂bpy (46.5 mg, 0.25 mmol) was added to a suspension of [Ru(PPh₃)₃(CO)(H)₂] (200 mg, 0.21 mmol) in EtOH (150 mL). The mixture was heated at reflux for 1 d under argon and then NH₄PF₆ (342 mg, 2.1 mmol) was added. The mixture was further heated at reflux for 1 h. The solvent was removed under reduced pressure and the pale-yellow solid was collected and washed with ice-cold methanol $(3 \times 4 \text{ mL})$. It was recrystallized by slow evaporation of diethyl ether into a CH₂Cl₂ solution of the complex. Yield 82.5 mg, 46.7 %. Elemental analysis calcd. (%) for $C_{49}H_{43}F_6N_2OP_3Ru$ (983.87): C 59.82, H 4.41, N 2.85; found C 59.76, H 4.53, N 2.71. IR (KBr): $\tilde{v} = v(Ru-H)$ 2001; ν (C=O) 1936; ν (P-F) 834 cm⁻¹. ESI-MS (positive): $m/z = 839 [M^+]$. ¹H NMR (300 MHz, CDCl₃): δ = 8.90 (d, J = 5.5 Hz, 1 H, bpy H), 8.01 (s, 2 H, bpy H), 7.56 (d, J = 5.6 Hz, 1 H, bpy H), 7.38-7.24 (m, 6 H, phenyl H), 7.29-7.34 (m, 12 H, phenyl H), 7.17-7.25 (m, 12 H, phenyl H), 6.44 (d, J = 5.7 Hz, 1 H, bpy H), 5.77 (s, 1 H, bpy H), 2.34 (s, 3 H, -CH₃), 2.28 (s, 3 H, -CH₃), -11.45 (t, J = 19.4 Hz, 1 H, Ru-H) ppm.



³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 45.7 (s, PPh₃), -144.4 (sept, PF₆⁻) ppm. UV/Vis (CH₃CN): λ_{max} /nm (ε /mol⁻¹ dm³ cm⁻¹): 267 sh (20980), 271 sh (20270), 290 sh (15620), 308 sh (11870), 396 (1470).

[Ru^{II}(Me₂Phen)(CO)(H)(PPh₃)₂]PF₆ (2): The synthetic method is similar to that of **1** except that the ligand Me₂Phen (52.1 mg, 0.25 mmol) was used instead of Me₂bpy. Yield 82.5 mg, 46.7 %. Yield 106.4 mg, 50.2 %. Elemental analysis calcd. (%) for C₅₁H₄₃F₆N₂OP₃Ru (1007.89): C 60.78, H 4.30, N 2.78; found C 60.86, H 4.41, N 2.75. IR (KBr): $\tilde{v} = v(Ru-H)$ 2026; v(C=O) 1937; v(P-F) 841 cm⁻¹. ESI-MS (positive): m/z = 863 [M^+]. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.44$ (d, J = 8.3 Hz, 1 H, phen H), 8.02 (t, J = 8.5 Hz, 2 H, phen H), 7.86 (d, J = 8.7 Hz, 1 H, phen H), 7.52 (d, J = 8.3 Hz, 1 H, phen H), 7.31–7.24 (m, 9 H, phenyl H), 7.20–6.95 (m, 21 H, phenyl H), 6.87 (d, J = 8.3 Hz, 1 H, phen H), 2.41 (s, 3 H, CH₃), 2.09 (s, 3 H, CH₃), -11.25 (t, J = 18.8 Hz, 1 H, Ru–H) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃): $\delta = 43.6$ (s, PPh₃), -144.2 (sept, PF₆⁻) ppm. UV/Vis (CH₃CN): λ_{max}/nm (ε/mol^{-1} dm³ cm⁻¹): 226 sh (59060), 275 sh (25090), 318 sh (7230), 395 (870).

[Ru^{II}(PhenCOOH)(CO)(H)(PPh₃)₂]PF₆ (3): Compound **3** was prepared by a procedure similar to that for **1**, except PhenCOOH (56.1 mg, 0.25 mmol) was used instead of Me₂bpy. Yield 84.6 mg, 45.8 %. Elemental analysis calcd. (%) for C₅₀H₃₉F₆N₂O₃P₃Ru (1023.85): C 58.66, H 3.84, N 2.74; found C 58.59, H 3.92, N 2.81. IR (KBr): $\tilde{v} = v(Ru-H) 2007; v(C=O) 1945; v(P-F) 841; v(C=O) 1618 cm⁻¹. ESI-MS (positive):$ *m/z*= 879 [*M* $⁺]. ¹H NMR (300 MHz, CDCl₃): <math>\delta$ = 9.45 (s, 1 H, -COOH), 8.35 (d, *J* = 7.6 Hz, 1 H, phen H), 8.14 (d, *J* = 8.8 Hz, 2 H, phen H), 7.73 (d, *J* = 8.6 Hz, 2 H, phen H), 7.58 (d, *J* = 8.1 Hz, 1 H, phen H), 7.24–7.31 (m, 12 H, phenyl H), 7.17–7.22 (m, 6 H, phenyl H), 7.05–7.14 (m, 12 H, phenyl H), 5.77 (s, 1 H, phen H), -12.09 (t, *J* = 19.9 Hz, 1 H, Ru–H) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 44.5 (s, PPh₃), -144.2 (sept, PF₆⁻) ppm. UV/Vis (CH₃CN): λ_{max}/nm (ε/mol⁻¹·dm³·cm⁻¹): 232 (38680), 270 sh (20220), 276 sh (19800), 325 sh (6160), 425 sh (1370).

[Ru^{II}(PhenCN)(CO)(H)(PPh₃)₂]PF₆ (4): PhenCN (51.5 ma. 0.25 mmol) was added to a suspension of [Ru(PPh₃)₃(CO)(H)₂] (200 mg, 0.21 mmol) in the presence of excess Et₂NH·HCl (169 mg, 2.1 mmol) in EtOH (150 mL). The mixture was heated at reflux for 1 d under argon and then NH₄PF₆ (342 mg, 2.1 mmol) was added. The mixture was heated at reflux for a further 1 h. The solvent was removed under reduced pressure and the pale-yellow solid was collected and washed with by water $(3 \times 4 \text{ mL})$ and then by icecold methanol (3×4 mL). It was recrystallized by slow evaporation of a CH₂Cl₂/MeOH (1:3, v/v) solution of the complex. Yield 80.6 mg, 44.6 %. Elemental analysis calcd. (%) for C₅₀H₃₈F₆N₃OP₃Ru (1004.85): C 59.76, H 3.81, N 4.18; found C 59.81, H 3.92, N 4.15. IR (KBr): v = ν (C=O) 1951; ν (P–F) 839 cm⁻¹. ESI-MS (negative): $m/z = 860 [M^+]$. ¹H NMR (300 MHz, CDCl₃): δ = 9.13 (d, J = 6 Hz, 1 H, phen H), 8.49 (dd, J = 15.8, 7.9 Hz, 2 H, phen H), 8.19 (d, J = 1.9 Hz, 2 H, phen H), 7.63 (dd, J = 7.8, 5.4 Hz, 1 H, phen H), 7.31-7.36 (m, 8 H, phenyl H), 7.10-7.22 (m, 22 H, phenyl H), 5.33 (s, 1 H, phen H), -10.43 (t, J = 18.5 Hz, 1 H, Ru–H) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 45.0 (s, PPh₃), -144.4 (sept, PF₆⁻) ppm. UV/Vis (CH₃CN): λ_{max}/nm (ɛ/mol⁻¹ dm³ cm⁻¹): 276 (37350), 290 sh (26010), 324 sh (9080), 378 (3640), 465 (1180).

[Ru^{II}(Me₂Ph₂phen)(CO)(H)(PPh₃)₂]PF₆ (5): The synthetic method used was similar to that of **1** except that the ligand Me₂Ph₂phen (90.1 mg, 0.25 mmol) was used instead of Me₂bpy. Yield 107.6 mg, 44.2 %. Elemental analysis calcd. (%) for C₆₃H₅₁F₆N₂OP₃Ru (1160.09): C 65.23, H 4.43, N 2.41; found C 65.20, H 4.60, N 2.49. IR (KBr): $\tilde{v} = \nu$ (Ru–H) 2032; ν (C=O) 1938; ν (P–F) 838 cm⁻¹. ESI-MS (positive): *m/z* = 1015 [*M*⁺]. ¹H NMR (300 MHz, CDCl₃): δ = 7.98 (d, *J* = 9.3 Hz, 1 H, phen H), 7.82 (d, *J* = 9.2 Hz, 1 H, phen H), 7.75–7.53 (m, 11 H, phenyl



H), 7.50 (m, 2 H, phen H), 7.46 (s, 1 H, phen H), 7.39–7.29 (m, 9 H, phenyl H), 7.23–7.10 (m, 18 H, phenyl H), 6.81 (s, 1 H, phen H), 2.46 (s, 3 H, -CH₃), 2.20 (s, 3 H, -CH₃), -11.09 (t, J = 18.8 Hz, 1 H, Ru–H) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃): $\delta = 43.5$ (s, PPh₃), -144.2 (sept, PF₆⁻) ppm. UV/Vis (CH₃CN): λ_{max} /nm (ϵ /mol⁻¹ dm³ cm⁻¹): 225 sh (61930), 248 sh (38270), 292 sh (33060), 330 sh (10270), 402 (2250).

[Ru^{II}(Ph₂Phen)(CO)(H)(PPh₃)₂]PF₆ (6): The synthetic method used was similar to that of **1** except that the ligand Ph₂Phen (83.5 mg, 0.25 mmol) was used instead of Me₂bpy. Yield 103.4 mg, 43.5 %. Elemental analysis calcd. (%) for C₆₁H₄₇F₆N₂OP₃Ru (1132.03): C 64.72, H 4.18, N 2.47; found C 64.80, H 4.26, N 2.35. IR (KBr): $\tilde{v} = v$ (C≡O) 1942; v(P–F) 838 cm⁻¹. ESI-MS (positive): m/z = 987 [M^+]. ¹H NMR (300 MHz, CDCl₃): $\delta = 9.22$ (d, J = 5.3 Hz, 1 H, phen H), 8.13 (d, J = 5.3 Hz, 1 H, phen H), 7.90 (dt, J = 9.4 Hz, 2 H, phen H), 7.67–7.54 (m, 8 H, phenyl H), 7.48 (dd, J = 7.6, 1.7 Hz, 2 H, phen H), 7.43–7.36 (m, 2 H, phen H), 7.37–7.29 (m, 8 H, phenyl H), 7.27–7.15 (m, 22 H, phenyl H), −11.00 (t, J = 19.1 Hz, 1 H, Ru–H) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃): $\delta = 46.1$ (s, PPh₃), −144.2 (sept, PF₆⁻) ppm. UV/ Vis (CH₃CN): λ_{max}/nm (ε/mol^{-1} dm³ cm⁻¹): 225 sh (55410), 289 sh (28950), 322 sh (12290), 401 sh (3690).

[Ru^{II}(dpq)(CO)(H)(PPh₃)₂]PF₆ (7): The synthetic method used was similar to that of **1** except that the ligand dpq (58.06 mg, 0.25 mmol) was used instead of Me₂bpy. Yield 111.8 mg, 51.6 %. Elemental analysis calcd. (%) for C₅₁H₃₉F₆N₄OP₃Ru (1031.87): C 59.36, H 3.81, N 5.43; found C 59.22, H 3.95, N 5.38. IR (KBr): $\tilde{v} = v$ (Ru-H) 2006; v(C=O) 1941; v(P–F) 840 cm⁻¹. ESI-MS (positive): m/z = 887 [M^+]. ¹H NMR (300 MHz, CDCl₃): $\delta = 9.38$ (d, J = 8.1 Hz, 1 H, dpq H), 9.29 (t, J = 6.7 Hz, 2 H, dpq H), 9.14 (dd, J = 4.1, 2.0 Hz, 2 H, dpq H), 8.13 (d, J = 5.5 Hz, 1 H, dpq H), 7.09 (dd, J = 8.2, 5.3 Hz, 1 H, dpq H), -11.15 (t, J = 19.2 Hz, 1 H, Ru–H) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃): $\delta = 46.1$ (s, PPh₃), -144.2 (sept, PF₆⁻) ppm. UV/ Vis (CH₃CN): λ_{max} /nm (ε/mol⁻¹ dm³ cm⁻¹): 2256 sh (47680), 298 sh (23600), 322 sh (6550), 401 (2500).

[Ru^{II}(dpqc)(CO)(H)(PPh₃)₂]PF₆ (8): The synthetic method used was similar to that of **1** except that the ligand dpqc (71.6 mg, 0.25 mmol) was used instead of Me₂bpy. Yield 114.7 mg, 50.3 %. Elemental analysis calcd. (%) for C₅₅H₄₅F₆N₄OP₃Ru (1085.97): C 60.83, H 4.18, N 5.16; found C 60.66, H 4.30, N 5.08. IR (KBr): $\tilde{v} = v$ (Ru–H) 1971; v(C=O) 1951; v(P–F) 841 cm⁻¹. ESI-MS (positive): m/z = 941 [M⁺¹. ¹H NMR (300 MHz, CDCI₃): $\delta = 9.35$ (d, J = 8.2 Hz, 1 H, dpqc H), 9.24 (d, J = 7.9 Hz, 1 H, dpqc H), 9.17 (d, J = 5.2 Hz, 1 H, dpqc H), 8.02 (d, J = 5.7 Hz, 1 H, dpqc H), 7.74 (dd, J = 8.3, 5.1 Hz, 1 H, dpqc H), 7.01 (dd, J = 8.2, 5.3 Hz, 1 H, dpqc H), 2.14 (m, 4 H, -CH₂), 1.56 (m, 4 H, -CH₂), −11.14 (t, J = 19.4 Hz, 1 H, Ru–H) ppm. ³¹P{¹H} NMR (162 MHz, CDCI₃): $\delta = 46.2$ (s, PPh₃), −144.2 (sept, PF₆⁻) ppm. UV/ Vis (CH₃CN): λ_{max}/nm ($\varepsilon/mol^{-1} dm^3 \cdot cm^{-1}$): 224 sh (50380), 268 sh (33460), 308 sh (15860), 342 sh (5653), 404 (1780).

[Ru^{II}(dppz)(CO)(H)(PPh₃)₂]PF₆ (9): The synthetic method used was similar to that of **1** except that the ligand dppz (70.6 mg, 0.25 mmol) was used instead of Me₂bpy. Yield 112 mg, 49.3 %. Elemental analysis calcd. (%) for C₅₅H₄₁F₆N₄OP₃Ru (1081.93): C 61.06, H 3.82, N 5.18; found C 61.17, H 3.95, N 5.02. IR (KBr): $\tilde{v} = v$ (Ru–H) 2019; v(C=O) 1939; v(P–F) 839 cm⁻¹. ESI-MS (positive): m/z = 937 [M^+]. ¹H NMR (300 MHz, CDCl₃): $\delta = 9.53$ (d, J = 7.2 Hz, 1 H, dppz H), 9.43 (d, J = 8.2 Hz, 1 H, dppz H), 9.32 (d, J = 5.1 Hz, 1 H, dppz H), 8.45 (dd, J = 6.6, 3.4 Hz, 2 H, dppz H), 8.15 (d, J = 4.3 Hz, 1 H, dppz H), 8.08 (dd, J = 6.6, 3.4 Hz, 2 H, dppz H), 7.88 (dd, J = 8.2, 5.2 Hz, 1 H, dppz H), 7.28–7.10 (m, 30 H, phenyl H), -11.19 (d, J = 19.1 Hz, 1 H, Ru–H) ppm. ³¹P{¹H} NMR (162 MHz, CDCl₃): $\delta = 46.0$ (s, PPh₃), -144.2 (sept, PF₆⁻) ppm. UV/Vis (CH₃CN): λ_{max}/nm





(ɛ/mol⁻¹·dm³·cm⁻¹): 225 sh (54850), 277 sh (55990), 312 sh (16940), 364 (10170), 412 (2920).

Physical Measurements and Instrumentation: ¹H NMR and ³¹P{¹H} NMR spectra were recorded with a Bruker AV300 (300 MHz) FT-NMR spectrometer. Chemical shifts (δ) are reported relative to tetramethylsilane (Me₄Si). All-positive-ion ESI mass spectra were recorded with a PE-SCIEX API 150 EX single-quadruple mass spectrometer. Elemental analysis was performed with an ElementarVario MICRO Cube elemental analyzer. IR spectra of the solid samples as KBr discs were obtained within the range 4000-400 cm⁻¹ with an AVATAR 360 FTIR spectrometer. All of the electronic absorption spectra were recorded with a Hewlett-Packard 8453 or Hewlett-Packard 8452A diode-array spectrophotometer. Steady-state emission and excitation spectra were measured at room temperature and at 77 K with a Horiba JobinYvon Fluorolog-3-TCSPC spectrofluorometer. The solutions were rigorously degassed with a highvacuum line in a two-compartment cell with not less than four successive freeze-pump-thaw cycles. The measurements at 77 K were carried out with dilute solutions of the samples in EtOH/MeOH (4:1, v/v) loaded in a guartz tube inside a guartz-walled Dewar flask that contained liquid nitrogen. Luminescence quantum yields were determined by using the optical dilution method described by Demas and Crosby^[40] with an aqueous solution of $[Ru(bpy)_3]Cl_2$ ($\phi_{em} =$ 0.042^[41] with 436 nm excitation) or with excitation at 350 and 345 nm by using quinine sulfate in 1 ${\rm M}$ H_2SO4 ($\phi_{\rm em}$ = 0.547 and 0.542^[42]) at room temperature as a reference. Luminescence lifetimes were measured by using the time-correlated single-photoncounting (TCSPC) technique with a Fluorolog-3-TCSPC spectrofluorometer in fast MCS mode with a Nano LED-375 LH excitation source, which had a peak excitation wavelength at 375 nm and a pulse width of less than 750 ps. The photon-counting data were analyzed with Horiba JobinYvon Decay Analysis Software.

Cyclic Voltammetry (CV): Measurements were performed with a CH Instruments, Inc. Model CHI 620 Electrochemical Analyzer. Electrochemical measurements were performed in MeCN solution with $[nBu_4N]PF_6$ (0.1 m) as the supporting electrolyte at room temperature. The reference electrode was a Ag/AgCl (0.1 m in MeCN) electrode and the working electrode was a glassy carbon electrode (CH Instruments, Inc.) with platinum wire as the counter electrode. The surface of the working electrode was polished with a 1 µm *a*-alumina slurry (Linde) and then with a 0.3 µm *a*-alumina slurry (Linde) on a microcloth (Buehler Co.). The ferrocenium/ferrocene^{+/0} couple (FeCp₂) was used as an internal reference. All of the solutions for the electrochemical studies were deaerated with pre-purified argon gas prior to the measurements.

X-ray Crystal Structure Determination: The crystal structures were determined with an Oxford Diffraction Gemini S Ultra X-ray single-crystal diffractometer by using graphite-monochromated Cu- K_{α} radiation ($\lambda = 1.5417$). The structures were solved by using direct methods with the SHELXS-97 program.^[43] The Ru atoms and many of the non-hydrogen atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were located after refinement by full-matrix least-squares by using the SHELXL-97 program.^[44] In the final stage of the least-squares refinement, all non-hydrogen atoms were refined anisotropically. H atoms were generated by using the SHELXL-97 program.^[19] The positions of the H atoms were calculated based on the riding model with thermal parameters that were 1.2 times that of the associated C atoms and participated in the calculation of the final *R* indices.

CCDC 1460787 (for **3**), 1460788 (for **7**), 1460786 (for **8**), and 1460789 (for **9**) contain the supplementary crystallographic data for this pa-

per. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Luminescent Ru Complexes

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Luminescent Carbonyl Hydrido Ruthenium(II) Diimine Coordination Compounds: Structural, Photophysical, and Electrochemical Properties





Luminescent carbonyl hydrido ruthenium(II) complexes with various diimine ligands have been synthesized. The effects of the electronic features and diimine ligand π -conjugation on the electronic and photophysical properties are discussed. The luminescence performance of these complexes could be significantly enhanced by increasing the rigidity and π -conjugation of the diimine ligand.

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