Reaction of Ru(tpy)Cl₃ with *N,N,C*-Terdentates, 3,2'-Annulated-6-(2''-pyridyl)-2-phenylpyridines

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The reactions of Ru(tpy)Cl₃ (tpy = 2,2';6',2''-terpyridine) with new *N,N,C*-terdentate ligands, 3,2'-annulated-6-(2''-pyridyl)-2-phenylpyridines (**1**, HL) and the properties of their Ru(II) complexes are described. The distribution ratio of the two possible Ru(II) complexes, a pentaaza-coordinated complex [Ru(tpy)(**1**-*N,N'*)Cl]⁺ and a cycloruthenated complex [Ru(tpy)(La-*N,N',C*)]⁺ are highly dependent on the length of the polymethylene unit. The trimethylene bridge of the *N,N,C*-terdentate in pentaaza-coordinated complex is rigid enough to induce an asymmetry in the complex.

Introduction

Cycloruthenated complexes of bidentate ligands such as 2-phenylpyridine and benzo[*h*]quinoline, presenting *N,C*-donor atoms to a metal center are extensively studied.[1] The interests of these compounds stem from the possible usage for photochemical and photophysical properties,[2] and also models for the development of synthetic methodology for the preparation of specific cyclometallated complexes.[3] The *N,N,C*-terdentate, 6-(2'-pyridyl)-2-phenylpyridine (**1a**, HLa) was introduced as a higher homology of the series. Additionally, cycloplatinated complexes of **1a** added intriguing properties including base-selective DNA cleavage activity,[4] which can be a useful probe to understand nucleic acids.

As far as the coordination chemistry is concerned, the reaction of **1a** with RuCl₃ did not form either bis-cycloruthenated [Ru(La-*N,N',C*)₂] or tris-complex [Ru(**1a**-*N,N'*)₃]²⁺, but instead afforded only a tetraazacoordinated complex [Ru(**1a**-*N,N'*)₂Cl₂].[5] On the other hand, the reaction of **1a** with Ru(tpy)Cl₃ afforded a non-cycloruthenated complex [Ru(tpy)(**1a**-*N,N'*)Cl]⁺ in which **1a** acts as a *N,N*-bidentate and a cycloruthenated complex [Ru(tpy)(La-*N,N',C*)]⁺ in which **1a** as a *N,N,C*-terdentate.[6] Formation of these two complexes could be explained by a stepwise coordination of a distal nitrogen, followed by a central nitrogen of the second ligand. There are two possible modes of attack for distal nitrogen of **1** onto the metal center of Ru(tpy)Cl₃ to result in two isomeric pentaaza-coordinated complexes **2** and **3** (Scheme 1), of which the intermediate **3** can only undergo cycloruthenation to **4**.

Related studies on the formation of ruthenium complexes by unsymmetrical *N,N,N*-terdentates revealed that an equatorial attack favors to form a pentaaza-coordinated Ru(II) complex [Ru(L-*N,N',N''*)(L-*N,N'*)Cl]⁺ when the additional stabilizing force, such as π-stacking is strong enough to prevent the complex from a backside displacement toward a hexaaza-coordinated complex [Ru(L-*N,N',N''*)₂]²⁺. The introduction of steric restriction on the unsymmetrical *N,N,N*-terdentate, however, forced the distal nitrogen to push out chloride from the metal core to adopt [Ru(L-*N,N',N''*)₂]²⁺ in
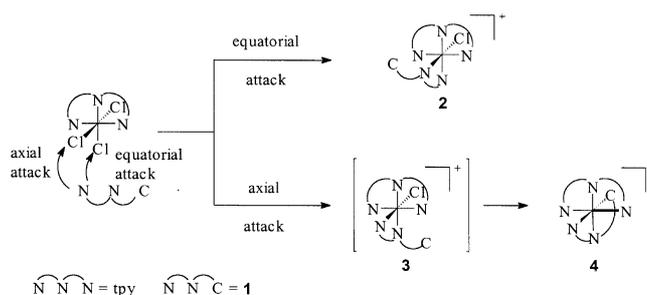
Scheme 1. Reaction mode of *N,N,C*-terdentate with Ru(tpy)Cl₃.

the presence of room light.[7] Although studies on cyclometallation have long been pursued, the conformational effect of the ligands was examined only in the limited cases.[1,8] We herein describe the reaction pattern and the steric effect of the *N,N,C*-terdentate ligands **1**, in which the *N,C*- bite-angles were controlled by annulating bridge at 3,2'-position, upon the reaction with Ru(tpy)Cl₃.
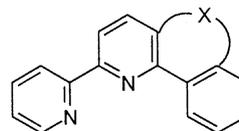
1a (HLa) X = H, H,   **1b** (HLb) X = -CH₂-,   **1c** (HLc) X = -(CH₂)₂-,
1d (HLd) X = -(CH₂)₃-, **1e** (HLe) X = -(CH₂)₄-, **1f** (HLf) X = -CH=CH-

Experimental Section

Melting points were determined using a Fischer-Jones melting points apparatus and are not corrected. Infrared (IR) spectra were obtained using a Perkin-Elmer 1330 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker-250 spectrometer 250 or 300 MHz for ¹H NMR and are reported as parts per million (ppm) from the internal standard tetramethylsilane (TMS). Chemicals and solvents were commercial reagents grade and used without further purification. Elemental analyses were take on a Hewlett-Packard Model 185B elemental analyzer. The starting materials **1b**, **1c**, **1d**, **1e**,[8c] 1-aminonaphthalene-

2-carbaldehyde (**6**)[9] and Ru(tpy)Cl₃[10] were prepared by either previously reported method or modification of such a method.

2-(2'-Pyridyl)benzo[*h*]quinoline (1f).   A mixture of 121 mg (1.0 mmol) of 2-acetylpyridine (**5**), 171 mg (1.0 mmol) of 1-aminonaphthalene-2-carbaldehyde (**6**), and 0.25 mL of saturated ethanolic KOH in 10 mL of absolute EtOH was refluxed for 8 h. The reaction mixture was poured into 100 mL of CH_2Cl_2 and washed with water, followed by brine. The organic layer was dried over anhydrous $MgSO_4$. Evaporation of the solvent afforded pale yellow solid, which was chromatographed on alumina, eluting with CH_2Cl_2 : hexane (7 : 3). The early fractions afforded 236 mg (95%) of **1f** as white platelets, mp 101-102 °C. ^{1}H NMR (300 MHz, CDCl₃) δ 9.48 (dd, J = 7.8, 1.5 Hz, H10), 8.89 (d, J = 7.8 Hz, H3'), 8.76 (dd, J = 4.5, 1.5 Hz, H6'), 8.70 (d, J = 8.4 Hz, H3), 8.29 (d, J = 8.4 Hz, H4), 7.93 (td, J = 7.8, 1.5 Hz, H4'), 7.92 (d, J = 7.8 Hz, H5/H6), 7.80 (t, J = 8.4 Hz, H8), 7.75-7.68 (m, 3H, H3, H6/H5, and H9), 7.39 (ddd, J = 8.4, 6.0, 1.0 Hz, H5'). Anal. Calcd. for $C_{18}H_{12}N_2$: C, 84.35; H, 4.72; N, 10.93. Found C, 84.38; H, 4.71; N, 10.91.

[Ru(tpy)(Lc-*N,N′,C*)](PF₆) (4c) and [Ru(tpy)(1c-*N,N′*)Cl](PF₆) (2c).   A mixture of 29.0 mg (0.065 mmol) of Ru(tpy)Cl₃ and 16.0 mg (0.065 mmol) of **1c** in 10 mL of HOAc was refluxed with 3 drops of *N*-ethylmorpholine for 2 h. The solvent was removed under reduced pressure, and the residue was dissolved in MeOH. The solution was filtered to remove any traces of unreacted Ru(tpy)Cl₃, and the filtrate treated with excess NH_4PF_6 to yield 45.0 mg (94%) of dark purple solid which was chromatographed on alumina eluting with toluene : CH₃CN (1 : 1). The early fractions afforded 20.0 mg of pink crystals as a [Ru(tpy)(Lc-*N,N′,C*)] (PF₆) after crystallization from the eluent. ^{1}H NMR (CD₃CN, 500 MHz) δ 8.57 (d, 2H, J = 8.0 Hz), 8.37 (overlapped td, 3H, J = 8.0, 1.5 Hz), 8.27 (d, 1H, J = 7.5 Hz), 8.01 (t, 1H, J = 7.5 Hz), 7.82-7.76 (m, 4H), 7.74 (td, 2H, J = 7.5, 0.8 Hz), 7.48-7.43 (m, 3H), 7.08-7.05 (m, 2H), 6.43(d, J = 7.7 Hz, H3' of **1c**), 6.39 (t, J = 7.7 Hz, H4' of **1c**), 5.46 (dd, 1H, J = 7.7, 1.4 Hz, H5' of **1c**), 3.26 (t, 2H, J = 7.5 Hz), 3.04 (t, 2H, J = 7.5 Hz). Anal. Calcd. for $C_{33}H_{24}N_5RuPF_6$: C, 53.81; H, 3.28; N, 9.51. Found C, 53.80; H, 3.30; N, 9.50. The latter fractions afforded 24.5 mg of purple crystals as [Ru(II)(tpy)(**1c**-*N,N′*)Cl](PF₆) after crystallization from the eluent. ^{1}H NMR (CD₃CN, 300 MHz) δ 10.04 (ddd, 1H, J = 5.7, 2.4, 0.8 Hz, H6" of **1c**), 8.54 (dd, 1H, J = 7.5, 1.0 Hz, H3" of **1c**), 8.32 (td, 1H, J = 7.5, 1.5 Hz, H4" of **1c**), 8.09 (d, 3H, J = 8.0 Hz, H5 of **1c**, H3' and H3" of tpy), 7.97-7.92 (m, 5H), 7.59 (t, 1H, J = 8.0 Hz, H4 of tpy), 7.53 (d, 1H, J = 7.5 Hz, H4 of **1c**), 7.43 (d, 2H, J = 4.8 Hz, H6' and H6" of tpy), 7.27-7.10 (m, 2H), 7.04 (td, 1H, J = 7.4, 1.0 Hz, H4' of **1c**), 6.96 (d, 1H, J = 6.2 Hz, H3' of **1c**), 6.56 (td, 1H, J = 8.0, 1.8 Hz, H5' of **1c**), 5.62 (dd, 1H, J = 8.0, 0.8 Hz, H6' of **1c**), 2.14 (s, 4H). Anal. Calcd. for $C_{33}H_{25}N_5RuClPF_6$: C, 51.27; H, 3.26; N, 9.06. Found C, 51.25; H, 3.25; N, 9.07.

[Ru(tpy)(1d-*N,N′*)Cl](PF₆) (2d).   The same procedure above described was employed with 54.4 mg (0.2 mmol) of Ru(tpy)Cl₃ and 88.1 mg (0.2 mmol) of **1d** in 10 mL of HOAc to give 137.0 mg (87%) of [Ru(tpy)(**1d**-*N,N′*)Cl]PF₆, which was chromatographed on alumina, eluting with CH₃CN : toluene (1 : 4). The recrystallization from the early fractions afforded dark purple crystals as a desired complex. ^{1}H NMR (CD₃CN, 500 MHz) δ 10.06 (ddd, 1H, J = 4.8, 1.5, 0.8 Hz, H6" of **1d**), 8.60 (d, 1H, J = 8.2 Hz, H3" of **1d**), 8.29 (td, 1H, J = 8.2, 1.5 Hz, H4" of **1d**), 8.28 (d, 1H, J = 8.0 Hz, H5 of **1d**), 8.22 (d, 1H, J = 8.1 Hz, H3' of tpy), 8.15 (d, 1H, J = 8.1 Hz, H3" of tpy), 8.12 (d, 1H, J = 5.4 Hz, H6' of tpy), 8.02 (d, 1H, J = 8.0 Hz, H3/H5 of tpy), 7.97 (td, 1H, J = 7.8, 1.4 Hz, H4' of tpy), 7.88 (ddd, 1H, J = 8.2, 4.8, 1.5 Hz, H5" of **1d**), 7.86 (d, 1H, J = 8.0 Hz, H5/H3 of tpy), 7.81 (td, 1H, J = 7.8, 1.5 Hz, H4" of tpy), 7.62 (t, 1H, J = 8.0 Hz, H4 of tpy), 7.52 (d, 1H, J = 8.0 Hz, H4 of **1d**), 7.45 (dd, 1H, J = 4.8, 1.5 Hz, H6" of tpy), 7.42 (ddd, 1H, J = 8.0, 4.8, 1.5 Hz, H5' of tpy), 7.17 (ddd, 1H, J = 8.0, 4.8, 1.5 Hz, H5" of tpy), 7.10 (td, 1H, J = 7.4, 1.0 Hz, H4' of **1d**), 6.82 (d, 1H, J = 6.2 Hz, H3' of **1d**), 6.59 (td, 1H, J = 7.4, 1.0 Hz, H5' of **1d**), 5.41 (d, 1H, J = 7.5 Hz, H6' of **1d**), 2.32 (dd, 1H, J = 13.2, 5.0 Hz), 2.21 (dd, 1H, J = 13.4, 6.7 Hz), 1.79-1.64 (m, 1H), 1.63-1.55 (m, 1H), 1.54-1.44 (m, 1H), 1.16-1.10 (m, 1H). Anal. Calcd. for $C_{34}H_{27}N_5RuClPF_6$: C, 51.88; H, 3.46; N, 8.90. Found C, 51.90; H, 3.45; N, 8.90.

[Ru(tpy)(1e-*N,N′*)Cl](PF₆) (2e).   The same procedure above described was employed with 29.0 mg (0.065 mmol) of Ru(tpy)Cl₃ and 18.6 mg (0.065 mmol) of **1e** in 10 mL of HOAc to give 66.0 mg (83%) of [Ru(tpy)(**1e**-*N,N′*)Cl]PF₆, which was chromatographed on alumina, eluting with CH₃CN : toluene (1 : 4). The recrystallization from the early fractions afforded dark purple crystals which turned out a mixture of two diasteromers. A major diastereomer: ^{1}H NMR (CD₃CN, 250 MHz) δ 10.06 (ddd, 1H, J = 4.8, 1.5, 0.8 Hz, H6" of **1e**), 8.65 (d, 1H, J = 8.2 Hz, H3" of **1e**), 8.38 (d, 1H, J = 8.3 Hz, H5 of **1e**), 8.26 (td, 1H, J = 8.2, 1.8 Hz, H4" of **1e**), 8.22 (d, 1H, J = 8.3 Hz, H3' of tpy), 8.16 (d, 1H, J = 8.3 Hz, H3" of tpy), 8.07 (dd, 1H, J = 7.5, 0.8 Hz, H6' of tpy), 8.00-7.78 (m, 5H, H5" of **1e**, H3, H5, and H4' and H4" of tpy), 7.66 (t, 1H, J = 7.5 Hz, H4 of tpy), 7.60 (d, 1H, J = 7.5 Hz, H4 of **1e**), 7.48 (ddd, 1H, J = 4.8, 1.5, 0.8 Hz, H6" of tpy), 7.35 (ddd, 1H, J = 7.4, 4.8, 1.0 Hz, H5' of tpy), 7.25-7.11 (m, 2H, H4' of **1e** and H5" of tpy), 6.78 (d, 1H, J = 6.2 Hz, H3' of **1e**), 6.54 (td, 1H, J = 7.4, 1.0 Hz, H5' of **1e**), 5.34 (dd, 1H, J = 7.5, 1.0 Hz, H5' of **1e**), 2.43 (dd, 1H, J = 12.5, 5.0 Hz), 1.81-1.61 (m, 2H), 1.36-1.26 (m, 1H), 1.10-0.94 (m, 2H), 0.92-0.80 (m, 2H). Anal. Calcd. for $C_{35}H_{29}N_5RuClPF_6$: C, 52.47; H, 3.65; N, 8.74. Found C, 52.50; H, 3.65; N, 8.76.

[Ru(tpy)(Lf-*N,N′,C*)]PF₆ (4f).   The same procedure described above was employed with 44.1 mg (0.1 mmol) of Ru(tpy)Cl₃ and 25.6 mg (0.1 mmol) of **1f** in 10 mL of HOAc to yield a purple solid, which was chromatographed on alumina eluting with toluene : CH₃CN (1 : 1). The early fractions afforded 61.0 mg (90%) of purple needles. ^{1}H NMR (300 MHz, CDCl₃) δ 8.64 (d, J = 8.4 Hz, H3 of tpy), 8.62 (d, J = 7.8 Hz, H3' of **1f**), 8.55 (d, J = 8.4 Hz, H3' of tpy), 8.50 (d, J = 8.4 Hz, H3' of **1f**), 8.40 (d, J = 8.1 Hz, H4 of **1f**), 8.08 (t, J = 7.8 Hz, H4 of tpy), 7.89 (AB quartet, H5 and H6 of **1f**), 7.69 (td, J = 8.0, 1.2 Hz, H4' of tpy), 7.59 (d, J = 5.4 Hz, H6' of **1f**),

7.28-7.14 (m, 4H), 7.07 (dd, $J = 5.4$, 1.2 Hz, H$_{5'}$ of tpy), 6.90 (d, $J = 7.2$ Hz, H$_7$ of **1f**), 6.86 (t, $J = 7.2$ Hz, H$_8$ of **1f**), and 5.98 (d, $J = 7.5$ Hz, H$_9$). Anal. Calcd. C$_{33}$H$_{22}$N$_5$RuPF$_6$: C, 53.96; H, 3.02; N, 9.53. Found C, 53.98; H, 3.03; N, 9.50.

Results and Discussion

Synthesis and Properties.   A new *N,N,C*-terdentate **1f** was prepared by Friedländer reaction of 2-acetylpyridine (**5**) and 1-aminonaphthalene-2-carbaldehyde[9] (**6**) in 95% yield. ^{1}H NMR of **1f** showed characteristic proton resonances for H10 and H6 as a doublet of doublet ($J_{9,10} = 7.8$, $J_{8,10} = 1.8$ Hz) at δ 9.45 and as a doublet of doublet ($J_{5',6'} = 4.8$, $J_{4',6'} = 1.5$ Hz) at δ 8.76, respectively.
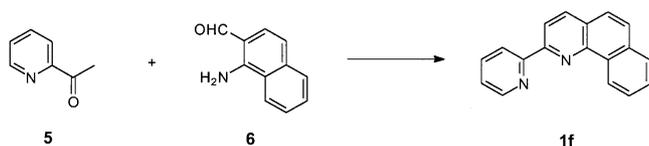
The reaction of an appropriate ligand with Ru(tpy)Cl$_3$ smoothly yielded two complexes type **2** and **4** which were characterized after anion metastasis with ammonium hexafluorophosphate. Distribution ratios of two complexes are highly dependent on the length of the bridging methylene units of the ligands. The two reaction products, a non-metallated, pentaaza-coordinated complex [Ru(tpy)(**1c**-*N*, *N'*)Cl]$^+$ and a cycloruthenated complex [Ru(tpy)(Lc-*N,N'*, *C*)]$^+$, were isolated from the reaction mixture of **1c** in a 3:2 ratio. This result is consistent with the previously reported result as in the case of **1a**.[6] The reactions of **1d** and **1e**, however, gave corresponding pentaaza-coordinated complexes as an only product while the reaction of **1f** gave only a cycloruthenated complex. It may not be surprising that reaction of **1b** afforded a messy, highly insoluble mixture which does not allow to isolate any of identifiable complex presumably due to unfavorable bite angle.[11]

Although it has been claimed that the solvent system affects the distribution ratio of a non-cyclometallated complex and a cycloruthenated complex,[6] we did not observe such a significant solvent effect in aqueous *vs.* nonaqueous solvent systems.

The dimethylene bridge system **1c** can attack Ru(tpy)Cl$_3$ either axial or equatorial fashion to give two complexes **2** and **4** as in the case of non-bridged parent **1a**. On the other hand, the tri- or tetramethylene bridge in the intermediate **3** from **1d** and **1e**, develops severe steric congestion around Ru(II) core thus interfering axial attack. Such a steric effect may induce dissociation of the ligand from **3** and reattack equatorially to form **2**. The equatorial attack, however, afforded a pentaaza-coordinated complex **2** in which the trimethylene bridge twisted the phenyl ring toward over the central pyridine ring of orthogonal tpy enough to create π-stacking between the two aromatic rings. Such a π-stacking not only stabilizes the complex but also creates a chiral axis through 2,1'-bond of **1d** by losing the flexibility of the trime-

thylene bridge.

In **4c**, cycloruthenation was confirmed by comparing ^{1}H NMR spectrum and elemental analysis with those of **2a**. Although ^{1}H NMR spectrum of **4c** is somewhat complex even in 500 MHz, all three protons of the benzene moiety were well resolved enough to be assigned. The H5' resonance of the ligand **1c** in complex **4c** appeared at 5.46 as a doublet of doublet ($J_{4',5'} = 7.7$, $J_{3',5'} = 1.4$ Hz) which is comparable to the value (δ 5.98) of H9 in **4f** which are well matched to the literature value (δ 5.69) of corresponding proton in **4a**.[6] Such resonances are highly upfield-shifted ($\Delta\delta$ 1.10 ppm) compared with that of H5' in complex **2c** due to neighboring C-Ru bond. On the other hand, **2c** showed two characteristic proton resonances at δ 10.04 ($J_{5'',6''} = 5.7$, $J_{4'',6''} = 2.4$, $J_{3'',6''} = 0.8$ Hz) for the H6'' of distal pyridine and at δ 5.62 ($J_{5'',6''} = 8.0$, $J_{4'',6''} = 0.8$ Hz) for H6' of the phenyl of **1c**. The former orients toward the electronic cloud of chlorine ligand on Ru(II) core, thus deshielded ($\Delta\delta$ 1.36 ppm), while the latter orients toward the shielding region of the central pyridine of tpy thus shifted upfield ($\Delta\delta$ 2.25 ppm) compared to the corresponding resonances of the free ligand.

The aliphatic region of ^{1}H NMR spectrum of **2d** revealed that the bridge is rigid enough to differentiate all the 6 protons showing 2 one-proton doublets of doublet at δ 2.32 ($^2J = 13.2$, $^3J = 5.0$ Hz) and δ 2.21 ($^2J = 13.4$, $^3J = 6.7$ Hz), and 4 well separated one-proton multiplets in the region of δ 1.79-1.12. Such a rigidity developed a chiral axis through 2,1'-bond to result in non-equivalence of the 11 protons of the 2,2';6',2''-terpyridine moiety, thus showing 21 aromatic proton resonances which were assigned by the double quantum COSY experiment (Figure 1).
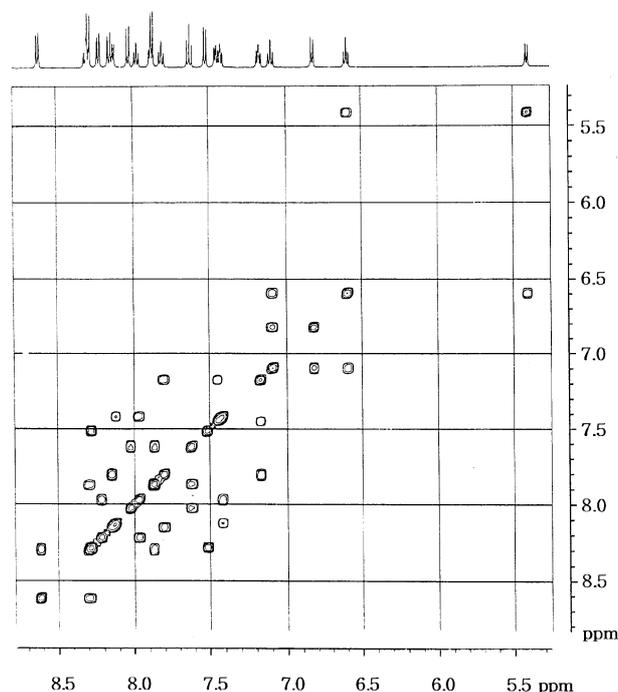
Figure 1. 500 MHz ^{1}H NMR COSY spectrum of Ru(tpy)(**1d**-*N,N'*)Cl][PF$_6$] (δ 5.30-8.80 ppm). (The peak at δ 10.06 was assigned by a separate decoupling experiment).

Table 1. UV Absorption Spectral Data of Ru(II) Complexes

Compound	$\lambda_{max}(\varepsilon)$ (CH$_3$CN)		
[Ru(tpy)(**1a**-N,N')Cl](PF$_6$)[a]	237(33,500)	278(27,100)	305(38,100)
	316(sh, 35,900)	502(10,700)	
[Ru(tpy)(**1c**-N,N')Cl](PF$_6$)	239(44,200)	277(39,700)	312(37,000)
	508(12,700)		
[Ru(tpy)(**1d**-N,N')Cl](PF$_6$)	234(26,700)	275(21,900)	315(29,600)
	500(7,000)		
[Ru(tpy)(**1e**-N,N')Cl](PF$_6$)	227(36,800)	272(37,600)	312(37,000)
	508(12,700)		
[Ru(tpy)(**La**-N,N',C)](PF$_6$)[a]	236(52,700)	274(sh, 46,800)	317(46,800)
	380(10,600)	512(13,800)	
[Ru(tpy)(**Lc**-N,N',C)](PF$_6$)	240(49,800)	276(47,000)	317(44,000)
	337(14,400)	399(10,500)	513(12,800)

[a]Data were taken from reference 6.

As reported previously,[7] the rigidity of a tetramethylene bridge of the ligand **1e** at room temperature induces a stereogenic axis through 2,1'-bond. In addition to such a stereogenic axis, the dissymmetry caused by forming [Ru(tpy)(**1e**-N,N')Cl]$^+$ resulted in diastermeric mixtures, which are confirmed by observation of a set of proton resonances in ^{1}H NMR spectrum and are not as yet separated.

In contrast to **1d** and **1e**, the reaction of planar **1f** afforded a cycloruthenated complex only. We reasoned that the planar naphthalene moiety not only develops severe steric congestion around the ruthenium core, but also is not able to deserve the stabilizing π-stacking between the two aromatic rings of two orthogonal ligands in **2**. Such a steric congestion of the benzo[*h*]quinoline moiety resulted in dissociation of ligand from the initially formed complex **2**, and then underwent an axial attack to form an intermediate **3** which underwent cycloruthenation.

Electronic Properties. UV absorption spectral data of the pentaaza-coordinated complex [Ru(tpy)(**1c**-N,N')Cl]$^+$ are summarized in Table 1, where the complexes showed four well-resolved absorption maxima in the ranges 220-240, 270-280, 312-316 and 500-513 nm with a similar extinction coefficient for each. Absorption bands in the range of 500-510 nm are tentatively assigned to MLCT transitions by comparison with known [Ru(tpy)(**1a**-N,N')Cl]$^+$. The more planar dimethylene bridged system showed higher intensity in all the absorption bands which reflects more conjugative interaction between the two adjacent aromatic rings. The most highly distorted tetramethylene bridged system, however, showed stronger intensity compared to those of trimethylene bridged system which may be due to the better π-stacking between the phenyl of the N,N,C-terdente ligand and central pyridine of the orthogonal tpy.

UV absorption spectrum of **4c** showed six absorption maxima, four of them were at 240, 276, 317, and 513 nm which were comparable to those of **2** while additional two appeared at 337, and 399 which is similar to those of **4a**. These additional absorption maxima also support the formation of cycloruthenated complex.

In conclusion, N,N,C-terdente ligands, 3,2'-polymethyl-

ene-6-(2''-pyridyl)-2-phenylpyridines (**1**, HL) were smoothly reacted with Ru(tpy)Cl$_3$ to afford two Ru(II) complexes, a pentaaza-coordinated [Ru(tpy)(**1**-N,N')Cl]$^+$ and a cycloruthenated [Ru(tpy)(L-N,N',C)]$^+$ whose ratio are highly dependent on the length of the polymethylene unit. The highly distorted ligands **1d** and **1e** formed the pentaaza-coordinated [Ru(tpy)(**1**-N,N')Cl]$^+$ while the most planar **1f** formed cycloruthenated [Ru(tpy)(L-N,N',C)]$^+$ as an only product. Steric congestions imposed by the tri- and tetramethylene bridge in the pentaaza-coordinated system develop chiral axis through 2,1'-bond upon complexation to result an asymmetry in the complex thus differentiate 11 proton resonances of tpy.

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