Intramolecular "CH···π(Metal Chelate Ring) Interactions" as Structural Evidence for Metalloaromaticity in Bis(pyridine-2,6-diimine)Ru^{II} Complexes

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Keywords: Metalloaromaticity / Ruthenium / CH···π interaction / Chelates

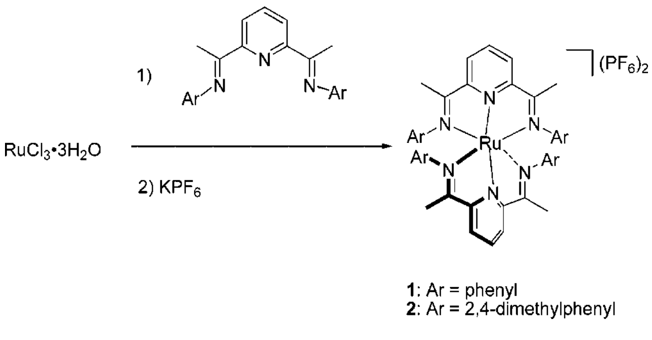
The synthesis and structural characterization of two novel Ru^{II} complexes (**1** and **2**) with tridentate pyridine-2,6-diimine ligands are described. In both compounds, *ortho*-CH bonds from the phenyl or phenyl-like rings produce unexpected CH···π interactions with ruthenium-α,α′-diimine chelate rings. This insight is thought to provide new structural evidence for the metalloaromaticity of the chelate rings in the ruthenium complexes studied. The molecular geometry of complex **1** is remarkably similar to S_4 symmetrical geometry, which is also a consequence of the four CH···π(chelate ring) interactions working cooperatively. In contrast, there are only two pairs of these interactions working in complex **2** because of the steric effects and electronic influences caused by the methyl-group substitutions.

Introduction

CH···π interactions are the weakest hydrogen bonds that operate between a soft acid CH and a soft or intermediate base π system.[1] It has been recognized that this kind of weaker and softer interaction plays significant roles in various fields of chemistry such as crystal packing,[2] host–guest chemistry,[3] self-assembly,[4] and chiral recognition.[5] As it is nonpolar and effective in water, the CH···π interaction is also especially important in biological systems.[6] In this broad context, the soft base π system, which acts as a CH acceptor, is comprised not only of an organic moiety such as a double bond, a triple bond or a delocalized aromatic ring,[7] but also of a metal−chelate ring of suitable transition-metal complexes that has been reported recently.[8] Zarić and coworkers[8] have reported ample evidence of this phenomenon based on new data as well as on a broad view of structures available in the CSD database. This interesting work represents a remarkable effort towards the definition of structural parameters for the interaction between C–H polar bonds and the whole of a π(metal-chelate ring) system. The concept of "metalloaromaticity" was proposed a long time ago[9] and it is well known that a large variety of transition metal chelate rings feature this metalloaromaticity.[10] Now we report for the first time additional evidence for ruthenium(II) complexes in which the ruthenium−diimine chelate ring could act as a CH acceptor. In this paper we describe the synthesis and structural characterization of ruthenium(II) complexes bearing two 2,6-bis(phenylimine)pyridine ligands. On the basis of the already known metalloaromaticity of ruthenium-α,α′-diimine chelate rings,[9] we report interesting and novel structural features concerning these 6N-coordinated complexes.

Results and Discussions

The tridentate 2,6-diimine-pyridine ligand, which was obtained by Schiff base condensation of 2 equiv. of aniline or 2,4-dimethyl-aniline with 2,6-diacetyl-pyridine,[11] reacted with $RuCl_3·3H_2O$ in an ethanol/water (1:1) solution under reflux followed by anion exchange, to afford the 2:1 complex $[RuL^1_2][PF_6]_2$ (**1**) or $[RuL^2_2][PF_6]_2$ (**2**) (Scheme 1).



Scheme 1.

Crystals of complexes **1** and **2** suitable for X-ray structure determination were grown at room temperature by li-

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DOI: 10.1002/ejic.200400864

quid diffusion of Et_2O into CH_3CN solutions. Details of data collection are listed in Table 1. Selected bond lengths and bond angles are listed in Table 2.[12]

Table 1. Crystallographic data for complexes **1** and **2**.

	1	2
Empirical formula	$C_{42}H_{40}F_{12}N_6OP_2Ru$	$C_{50}H_{56}F_{12}N_6O_{0.50}P_2Ru$
Formula mass	1035.81	1140.02
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
a [Å]	9.940(2)	27.384(6)
b [Å]	11.438(2)	15.926(3)
c [Å]	22.029(4)	24.620(5)
α [°]	95.60(3)	90.00
β [°]	99.14(3)	98.63(3)
γ [°]	111.07(3)	90.00
V [Å^3]	2274.8(8)	10616(4)
Z	2	8
$D_{calcd.}$ [g cm^{-3}]	1.512	1.427
μ [cm^{-1}]	0.504	0.439
T [K]	293 (2)	293(2)
λ [Å]	0.71073	0.71073
R_1	0.0827	0.0792
wR_2	0.1352	0.2190

Table 2. Selected bond lengths [Å] and angles [°] for complexes **1** and **2**.

	1	2
Bond lengths		
Ru–N1	2.099(8)	2.088(6)
Ru–N2	1.960(8)	1.976(5)
Ru–N3	2.062(9)	2.104(5)
Ru–N4	2.060(8)	2.123(5)
Ru–N5	1.962(8)	1.978(5)
Ru–N6	2.058(8)	2.083(5)
Bond angles		
N1–Ru–N2	77.2(3)	77.3(2)
N1–Ru–N3	154.7(3)	153.4(2)
N1–Ru–N4	93.2(3)	90.0(2)
N1–Ru–N5	106.6(3)	95.8(2)
N1–Ru–N6	93.9(3)	96.9(2)
N2–Ru–N3	77.6(4)	77.0(2)
N2–Ru–N4	102.3(3)	112.0(2)
N2–Ru–N5	176.3(4)	168.2(2)
N2–Ru–N6	102.8(3)	94.8(2)
N3–Ru–N4	92.5(3)	93.5(2)
N3–Ru–N5	98.7(4)	110.7(2)
N3–Ru–N6	91.3(3)	91.7(2)
N4–Ru–N5	77.6(4)	77.2(2)
N4–Ru–N6	154.9(3)	153.2(2)
N5–Ru–N6	77.2(4)	76.4(2)

The asymmetric unit of compound **1** consists of a complex cation, two hexafluorophosphate anions, and one noncoordinated water molecule, as shown in Figure 1. The most noteworthy structural feature of complex **1** is that one *ortho*-H from each phenyl ring points towards the center of the corresponding ruthenium-α,α′-diimine chelate ring (Figure 2). Comprehensive analysis was carried out with the program PLATON,[13] and relevant structural parameters, defined as shown in Figure 3, are listed in Table 3. The H-ring centroid (H···Cg) and H···ring plane (H···⊥) distances are in the range of 2.79–3.00 Å and 2.79–2.95 Å, respectively, and the γ angles usually have values below 10°. These data are similar to those (H···Cg distance <3.0 Å and γ <12.5°) reported for CH···π interactions with chelate rings[8] and indicate that CH···π interactions occur between *ortho*-CH bonds and the whole of an electronically delocalized ruthenium chelate ring in complex **1**. The C–H···Cg angles, 125, 102, 103, and 108°, are still below the optimal value (180°) for the strongest CH···π interaction, which may be due to the steric constraints in the molecule. On the basis of the reported metalloaromaticity of benzoquinonediimine ruthenium complex,[10] this kind of CH···π(planar chelate ring) interaction in complex **1** is thought to be a new kind of structural evidence for the metalloaromaticity of such planar chelate rings.

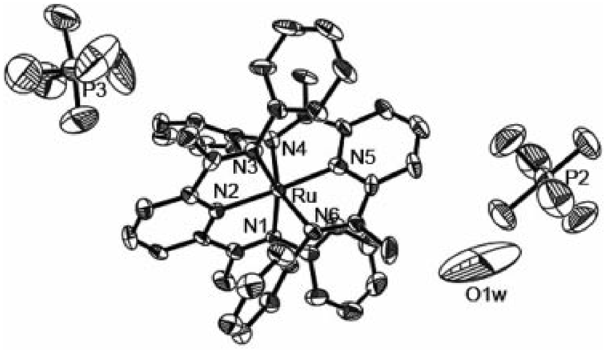

Figure 1. ORTEP drawing of compound **1** with thermal ellipsoids shown at the 30% level; hydrogen atoms were omitted for clarity.

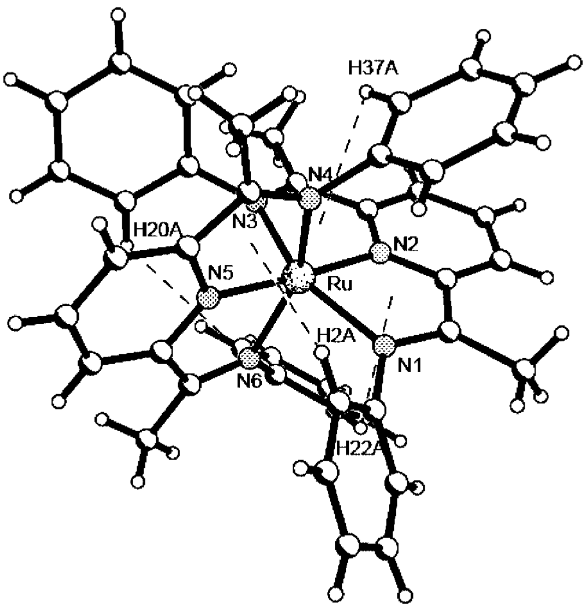

Figure 2. Four pairs of intramolecular "CH···(chelate ring)" interactions [C2H2A−(RuN4N5), C20H20A−(RuN5N6), C22H22A−(RuN1N2), and C37H37A−(RuN2N3)] work cooperatively in complex **1**.

Interestingly, it seemed that complex **1** belonged to a similar S_4 space group, but actually the complex ion $[RuL^1{}_2]^{2+}$ has a crystallographic C_1 symmetry, and the ruthenium atom has a slightly distorted octahedral geometry with *cis* angles at Ru^{II} of 77.2(3), 77.6(4), 92.5(3), 77.6(4), and

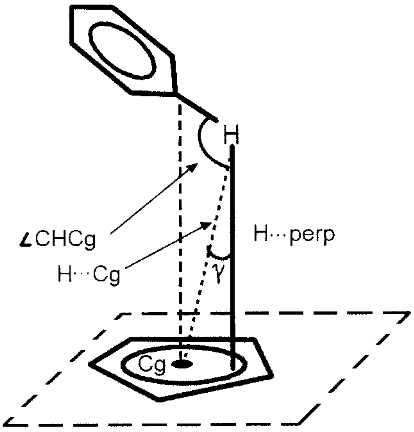

Figure 3. Cg is the centroid of the ruthenium chelate ring; γ is the angle defined by the H···Cg line and perpendicular H···(ring plane) line.

77.2(4)°. Geometry optimization calculations were carried out by the DFT method, and the result at the B3LYP/(LanL2DZ+3-21G*) level[14] proved that the optimized cation $[\mathrm{RuL}^1{}_2]^{2+}$ indeed exhibited an S_4 space group, which may be a consequence of the four pairs of CH···(chelate ring) interactions working cooperatively.

It is also worth mentioning that the average distances of Ru–N(pyridine) bonds [1.961(8) Å] and Ru–N(imine) bonds [2.070(8) Å] in complex **1** are shorter than those reported [1.992(3) Å and 2.140(3) Å, respectively] for the ruthenium complex with a tridentate pyridine-2,6-diimine ligand.[15] It is strongly suggested that the compact and stable structure of **1** is achieved by a cooperation of intramolecular CH···π interactions.[8]

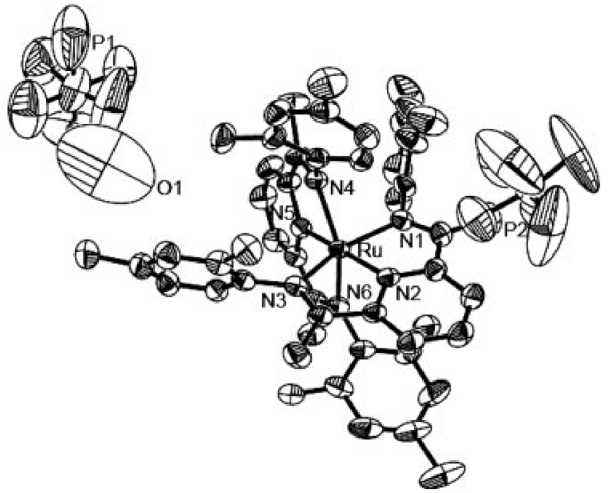

Figure 4. ORTEP drawing of complex **2** with thermal ellipsoids shown at the 30% level; hydrogen atoms were omitted for clarity.

The crystal structure of complex **2** seems to be more complicated and asymmetrical because of the 2- and 4-substituted methyl groups in the phenyl-like rings, as shown in Figure 4. However, the existence of one *ortho*-H per phenyl-like ring in **L²** could enable the formation of intramolecular CH···π interactions similar in nature to those found in complex **1**, but limited to two pairs of CH···(ruthenium-α,α′-diimine chelate ring) interactions, as shown in Figure 5. The difference between complexes **1** and **2** is attributed to the interligand steric repulsions and the electronic effects caused by the additional methyl groups.[1]

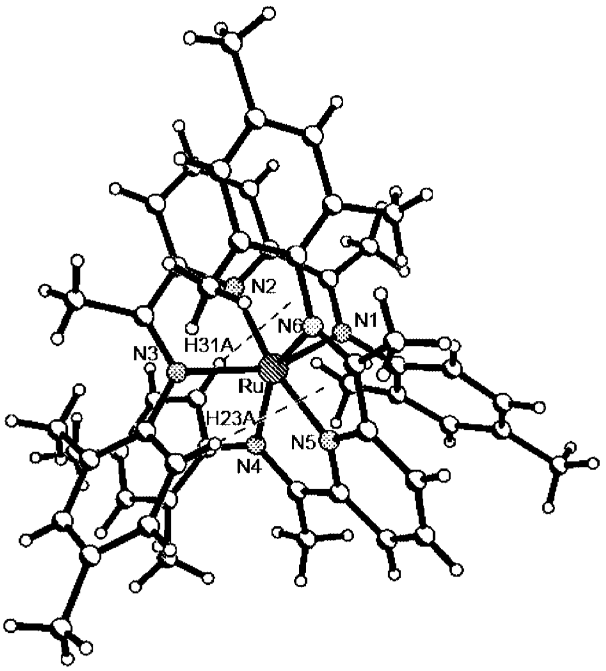

Figure 5. Only two pairs of intramolecular "CH···(chelate ring)" interactions [C23H23A–(RuN5N6) and C31H31A–(RuN1N2)] work cooperatively in complex **2**.

Conclusions

Intramolecular CH···π(chelate ring) interactions between ligand-aryl C–H bonds and ruthenium(II)-α,α′-diimine chelate rings are observed by X-ray crystal structural analysis of complexes **1** and **2**. To the best of our knowledge, this is the first time that these intramolecular CH···π(chelate ring)

Table 3. Intramolecular "CH···π(chelate ring)" interaction parameters for complexes **1** and **2**.

	CH-chelate ring	H···Cg [Å]	H···(ring plane) [Å]	C–H···Cg [°]	Γ [°]
C1	C2H2A–(RuN4N5)	2.79	2.79	125	2.67
	C20H20A–(RuN5N6)	2.97	2.93	102	9.39
	C22H22A–(RuN1N2)	3.00	2.95	103	10.07
	C37H37A–(RuN2N3)	2.92	2.91	108	5.26
C2	C23H23A–RuN5N6	2.89	2.86	126	1.53
	C31H31A–RuN1N2	2.85	2.82	136	6.92

interactions are used to feature the metalloaromaticity of such Ru^{II}-α,α′-diimine chelate rings.

Experimental Section

General: ^1H, ^{13}C NMR spectra were recorded with a JOEL JNM-ECA300 spectrometer. IR spectra were recorded with an AVATAR FTIR ESP spectrophotometer. ESI-MS spectra were obtained with a Bruker Esquire-LC/MSn spectrometer. Elemental analyses were carried out with a FlashEA1112 microanalyzer. The starting material $RuCl_3·3H_2O$ was purchased from Aldrich; the ligands 2,6-bis{1-(phenylimine)ethyl}pyridine (**L^1**) and 2,6-bis{1-[(2,4-dimethylphenyl)imine]ethyl}pyridine (**L^2**) were prepared according to the literature method.[11]

Preparation of $[RuL^1{}_2][PF_6]_2$: A solution of **L^1** (156 mg, 0.498 mmol) and $RuCl_3·3H_2O$ (50 mg, 0.241 mmol) in ethanol/water (1:1) (20 mL) was refluxed under nitrogen for 24 h until the solution became red or purple. After cooling, the insoluble materials were removed by filtration, and the complex was precipitated by the addition of saturated KPF_6 aqueous solution (5 equiv.). The complex was purified by chromatography on silica gel. It was eluted with CH_3CN/H_2O (25:1). The second fraction afforded $[RuL^1{}_2][PF_6]_2$ as an orange solid (76 mg, 31%). ESI-MS: *m/z* (%) = 364 $\{M - 2PF_6\}^{2+}/2$. $C_{42}H_{38}F_{12}N_6P_2Ru·H_2O$ (M_r = 1035.81): calcd. C 48.70, H 3.89, N 8.11; found C 48.66, H 4.05, N 7.96. ^1H NMR ([D$_3$]acetonitrile): δ = 2.61 (s, 12 H, CH_3), 6.39 (d, ^3J(H,H) = 6.54 Hz, 8 H, aromatic protons), 7.20 (m, 12 H, aromatic protons), 7.92 (t, 2 H, py), 8.11 (d, ^3J(H,H) = 7.92 Hz, 4 H, py). ^{13}C NMR ([D$_3$]acetonitrile): δ = 18, 120, 128, 130, 134, 144, 154, 177. IR (KBr): $\tilde{\nu}$ = 3420 (O–H), 1697 (C=N), 846 cm^{-1} (P–F).

Preparation of $[RuL^2{}_2][PF_6]_2$: A solution of **L^2** (146 mg, 0.395 mmol) and $RuCl_3·3H_2O$ (40 mg, 0.193 mmol) in ethanol/water (1:1) (20 mL) was refluxed under nitrogen for 48 h until the solution became red or purple. After cooling, the insoluble materials were removed by filtration, and the complex was precipitated by the addition of saturated KPF_6 aqueous solution (5 equiv.). The complex was purified by chromatography on silica gel. It was eluted with CH_3CN/H_2O (25:1). The second fraction afforded $[RuL^2{}_2][PF_6]_2$ as an orange−red solid (34 mg, 16%). ESI-MS: *m/z* (%) = 420 $\{M - 2PF_6\}^{2+}/2$. $C_{50}H_{56}F_{12}N_6O_{0.50}P_2Ru$ (M_r = 1140.02): calcd. C 52.68, H 4.95, N 7.37; found C 53.07, H 4.99, N 7.82. ^1H NMR ([D$_3$]acetonitrile): δ = 2.22–2.07 (m, 30 H), 2.65 (s, 6 H), 5.29–5.36 (m, 1 H), 5.77–6.11 (m, 3 H), 6.44 (m, 1 H), 6.57–6.85 (m, 7 H), 7.84–7.94 (m, 2 H), 7.95 (t, 2 H), 8.38–8.41 (m, 2 H). ^{13}C NMR ([D$_3$]acetonitrile): δ = 14, 16, 19, 29, 121, 123, 127, 128, 132, 134, 138, 145, 154, 174, 178. IR (KBr): $\tilde{\nu}$ = 3421 (O–H), 1635 (C=N), 841 cm^{-1} (P–F).

Acknowledgments

We thank the National Natural Science Foundation of China (20172032) (20372041) for supporting this work. We also thank Dr. Biao Wu (Institute of Chemistry, Chinese Academy of Sciences) for his help in the measurement of crystals. We are grateful to Prof. Guoshi Wu (Department of Chemistry, Tsinghua University) for his help in some of the calculations.

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Received: October 14, 2004