Half-Sandwich Rhodium and Iridium Fragments and Carboxylate Ligands as Building Blocks for the Formation of Metallamacrocycles

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ABSTRACT: A series of half-sandwich rhodium and iridium complexes containing carboxylate ligands were synthesized and characterized. Reactions between $[\text{Cp}^*\text{MCl}_2]_2$ ($\text{M} = \text{Ir}$ or Rh) and 1,3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (**L1**) gave binuclear complexes **1** and **2** under different conditions. The half-sandwich iridium and rhodium metallamacrocycles complexes **3-5** were constructed in a stepwise manner by the addition of carboxylate ligands (sodium acetate or the conjugate bases of pyrazine-2,3-dicarboxylic acid or 3-(2-pyridyl)acrylic acid) to the solution of the binuclear precursors prepared from the reactions of $[\text{Cp}^*\text{MCl}_2]_2$ ($\text{M} = \text{Rh}$ or Ir) with linear N,N'-donor ligands (4,4'-bipyridine or *trans*-1,2-bis(4-pyridyl)ethylene), respectively. The structures of binuclear complexes and tetranuclear macrocycles were confirmed by elemental analysis, IR, ^1H NMR spectroscopy and single-crystal X-ray diffraction.

Keywords: macrocycles • half-sandwich metal complexes • rhodium complexes • iridium complexes

Introduction

Over the past two decades, coordination-driven self-assembly has been used as an efficient way to construct a wide range of supramolecular metallacycles. [1-5] One of the principal objectives of supramolecular chemistry is to create nanoscale structures by exerting control over the ligand sizes and shapes, and to be able to utilize the unique properties of the assemblies. [6] A small change in the ligand can produce a major effect on the self-assembled structure. Therefore, controlling or tuning the structure, which provides an understanding of self-assembly processes and the properties of the supramolecular species, is still a challenging goal. [7-9] As recent research has revealed, self-assembled macrocycles which contain Cp^*M ($\text{M} = \text{Ir}, \text{Rh}$) or (*p*-cymene)Ru groups can be controlled by choosing appropriate bridging N-heterocyclic linkers and carboxylate ligands. [10, 11] The groups of Stang [12, 13], Davies [14], and others [15, 16] have pioneered the use of “chelating and bridging ligands” towards self-assembly. Ligands with two pairs of chelating sites linking two metal atoms, including $\text{N}^{\wedge}\text{N}\text{--}\text{N}^{\wedge}\text{N}$, $\text{O}^{\wedge}\text{O}\text{--}\text{O}^{\wedge}\text{O}$, and $\text{O}^{\wedge}\text{N}\text{--}\text{O}^{\wedge}\text{N}$ were investigated. [17-20] An enormous range of structures are available by using different metals and coordinating sites, many of which potentially have useful properties, such as electrochemical activity, host-guest chemistry, redox activity, magnetic behavior, etc. [21-24]

In this work, binuclear half-sandwich complexes based on $\text{Cp}^*\text{Ir}/\text{Cp}^*\text{Rh}$ units have been used as building blocks. These half-sandwich units have advantages in solubility, thermal stability and flexibility in fine-tuning processes, and therefore are suitable candidates for metallosupramolecular assembly. [25-26] Due to these advantages, a series of bi- and tetranuclear rhodium and iridium complexes (**1-5**) were synthesized and characterized.

Herein we also describe a ring opening reaction of **L1**, shown in Scheme 1. This result supports a similar reaction reported by Bu et al. [27] who used copper(II) complexes with **L1** to arrive at a tetranuclear complex with a $\text{N}^{\wedge}\text{N}\text{--}\text{N}^{\wedge}\text{N}$ coordination motif. The synthesis of compound **L2** is analogous to that observed by the group of Bu – the carbon center activated by coordination of the imino nitrogen

is very susceptible to nucleophilic attack by H₂O and/or adventitious amounts of H₂O present in the solvent. The heterocyclic compound **L1** reacts with H₂O, promoting the transformation to **L2**. [28]

Scheme 1 Mechanism for the hydrolysis of **L1** and the formation of **L2**.

2. RESULTS AND DISCUSSION

2.1 Binuclear cyclometalated complexes **1** and **2**

As shown in Scheme 2, **L1** was treated with [Cp*IrCl₂]₂ in a ratio of 1:1 in MeOH at room temperature in the presence of AgOTf to afford the binuclear complex **1**. These considerations led us to investigate the possibility of obtaining a half-sandwich rhodium complex with the same ligand. **L1** was treated with [Cp*RhCl₂]₂ in a ratio of 1:1 in the presence of THF containing a small amount of water. At this point, AgOTf was added and the mixture was stirred in the dark for 12 h to afford the binuclear rhodium complex **2** by a ring-opening reaction.

Scheme 2 Formation of complexes **1** and **2**.

Figure 1 shows the molecular structures of **1** and **2** and their cyclic voltammograms. Both complexes are binuclear, with one available coordination sites at each metal center, with each metal coordinated by two Cp* units. The Ir-N bonds of complex **1** were found to range from 2.069 to 2.104 Å (Figure 1a), while the Rh-N bond lengths of complex **2** are 2.094 and 2.167 Å (Figure 1b). The M-M distances are 6.410 (complex **1**) and 5.214 Å (complex **2**). In Figure 1b, the non-coordinated carbonyl oxygen atoms exhibit typical double bond distances of 1.260 Å. Long Rh1-N2 (2.167 Å) and Rh2-N3 bonds (2.125 Å) were found in the five-membered chelate rings.

Cyclic voltammetry of the binuclear complexes was carried out in a CH₂Cl₂/0.1 M Bu₄NPF₆ solution. Oxidation processes are observed for complexes **1** and **2**, with the first oxidation step in both complexes (at 0.53 and 0.50 V, respectively) is reversible. The second oxidation step of complex **2** is electrochemically irreversible, as can be seen from the current maxima of the forward and the reverse peaks for this step (Figure 1c, d).

Figure 1 a) and c) Molecular structure and cyclic voltammogram of complex **1**; b) and d) Molecular structure and cyclic voltammogram of complex **2** (gray for C, blue for N, red for O, dark green for Rh or Ir, green for Cl, all hydrogen atoms were omitted for clarity).

2.2 Synthesis and characterization of complexes **3** and **4**

The synthesis of complexes **3** and **4** is depicted in Scheme 3. $[\text{Cp}^*\text{RhCl}_2]_2$ was treated with *trans*-1,2-bis(4-pyridyl)ethylene (bpe) in a 1:1 molar ratio at room temperature, followed by four equivalents of AgOTf at room temperature overnight in the presence of NaOAc, providing **3**. Complex **4** was obtained in high yield by treating binuclear 4,4'-bipyridine(bpy)-bridged rhodium complexes with pyrazine-2,3-dicarboxylic acid in a 1:1 molar ratio at room temperature. The crystallographic data of complexes **3** and **4** are summarized in Table 1.

Scheme 3 Formation of complexes **3** and **4**.

In Figure 2a, the Rh1A···Rh2A and Rh1A···Rh2B bond lengths of **3** are 13.6149 and 3.8040 Å, respectively. As a consequence, the two ethylene groups are nearly parallel to each other, with a distance between the ethylene centroids of 3.7974 Å. The pyridyl rings were also found to be parallel to each other. In these complexes, the distances between the two pyridyl-based ligands are small because of the presence of π - π interactions and fall within the range required for [2 + 2] photoreaction. When crystals or a powdered crystalline sample of complex **3** was subjected to UV irradiation using an Hg lamp for a period of approximately 48 h, no dimerization was observed to occur by ^1H NMR spectroscopy. In Figure 2b, the Rh1···Rh2 and Rh1···Rh3 distances are 11.2707 and 6.9357 Å and these values are significantly smaller than those of **3**. Complex **4** showed that each Rh atom was coordinated by two nitrogen atoms of the 4,4'-bipyridine and pyrazine ligands, and one carboxylate oxygen atom from the pyrazine-2,3-dicarboxylate acid ligand. The N-Rh-O angle of **4** is 77.47°, and the Rh1A-N1B, Rh1A-N1A, Rh1A-O1A distances are 2.1236, 2.1170, 2.0695 Å, respectively. In conclusion, a concise method has been developed to functionalize carboxylate ligands under mild conditions, which can be used to assemble supramolecular nanochannel architectures.

Figure 2. a) and c) Molecular structure and cyclic voltammogram of complex **3**; b) and d) Molecular structure and cyclic voltammogram of complex **4** (gray for C, blue for N, red for O, dark green for Rh, green for Cl, all hydrogen atoms were omitted for clarity).

An oxidation process was seen for **3** at around 0.43 V in CH₂Cl₂/0.1 M Bu₄NPF₆. On the reductive side, complex **3** displays a reduction step where the forward wave is seen at 0.33 V (Figure. 2c). In Figure 2d, redox waves for complex **4** were observed ranging from -0.88 to 0.81 V.

2.3 Synthesis and characterization of complex **5**

Scheme 4 Formation of complex **5**.

Self-assembly of the zigzag complex **5** was achieved through combination of a binuclear bpy-bridged iridium complex and followed by four equivalents of AgOTf at room temperature overnight and two equivalents of 3-(2-pyridyl) acrylic acid, with addition of an excess of sodium acetate (Scheme 4). Complex **5** was characterized by IR, NMR, elemental analysis and single-crystal X-ray diffraction. The molecular structure of **5** (Figure 3a) shows that each 3-(2-pyridyl)acrylate ligand is bound to two iridium atoms, through double-site C-H activation involving σ -coordination to the olefin group. The two bpy ligands are orthogonal to the planes made by the two iridium atoms and the carboxylate ligands. In fact, Ir3 is coordinated by two atoms(N3 and O3) of the 3-(2-pyridyl)acrylate sodium salt bridging in an asymmetric mode with two ions belonging to distinct binuclear units (Ir3-N3 = 2.0810 Å, Ir1-O3 = 2.0994 Å).

In the zigzag structure shown in Figure 3b, the Na...Na distances are 12.8891 and 12.4049 Å.

Each Na ion is hexacoordinate, each sodium atom is ligated by six oxygen atoms, two from each macrocycle (Na1-O3 = 2.3419 Å; Na1-O4 = 2.4914 Å), and two from H₂O molecules. This may indicate that the C-H activation and self-assembly of the metallacycle formation is cooperative, thus giving rise to a 1D coordination polymer.

Figure 3 a) Molecular structure of complex **5**; b) Schematic of the zigzag structure, with the blue circles representing Na ions; c) Space-filling model of the 1D macrocycles linked by metal ions (gray for C, blue for N, red for O, dark green for Ir, green for Cl, all hydrogen atoms were omitted for clarity).

3. CONCLUSIONS

In summary, we have used half-sandwich rhodium and iridium complexes with nitrogen-donor or carboxylate ligands to construct organometallic binuclear complexes and tetranuclear macrocycles. In one case, **L1** underwent ring-opening under mild conditions [29]. We have shown that all of the macrocycles lead to different shapes in their self-assembled structures. These differences depend on several factors: the nature of the metal centers, the shape of the linker ligand, the donor types and so on. [30] In specific templated assemblies of metallamacrocycles, the coordination model of the metal is the main factor that determines the nuclearity and geometry of the macrocycle formed. Because of this,

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the amount of sodium acetate and the solvent used for crystallization was found to promote the formation of complex **5**.

4. EXPERIMENTAL SECTION

The starting materials $[\text{Cp}^*\text{MCl}_2]_2$ ($\text{M} = \text{Rh}, \text{Ir}$) were prepared by literature methods [31], while other chemicals were obtained commercially and used without further purification. All manipulations were performed using standard Schlenk techniques under an atmosphere of nitrogen. However, once the reactions were completed, subsequent work-up was performed without precaution, as the compounds are air-stable. Elemental analyses were performed on an Elementar III Vario EI analyzer. IR (KBr) spectra were recorded on the Nicolet FT-IR spectrophotometer. ^1H NMR spectra (400 MHz) were measured on a Bruker DMX-500 spectrometer in CDCl_3 (δ 7.26) or CD_3OD (δ 3.31).

Synthesis of complex **1**

A mixture of $[\text{Cp}^*\text{IrCl}_2]_2$ (80.0 mg, 0.1 mmol), and **L1** (23.6 mg, 0.1 mmol) in MeOH (10 mL) was stirred for 8 h, then AgOTf (51.2 mg, 0.2 mmol) was added to the solution and the reaction was stirred in the dark for 12 h. The solution was concentrated to give a dark red solid, which was washed with diethyl ether and dried under vacuum. X-ray quality crystals for complex **1** were obtained by slow diffusion of diethyl ether into methanol. Yield: 99.3 mg (91%). Anal. Calcd (%) for $\text{C}_{35}\text{H}_{49}\text{N}_6\text{O}_3\text{Cl}_3\text{Ir}_2$: C 38.47, H 4.52, N 7.69. Found: C 38.84, H 4.73, N 7.88. IR (KBr disk): 3421(w), 2360(w), 1650(w), 1449(s), 1415 (s), 1267(s), 1245(w), 1178(s), 1079(w), 1018(w), 784(m), 646(w) cm^{-1} . ^1H NMR (400 MHz, CD_3OD , ppm): δ = 8.87-8.74 (d, 2H, Py-H), 8.44-8.30 (d, 2H, Py -H), 8.21-8.00 (d, 2H, Py -H), 7.91-7.59 (d, 2H, Py -H), 1.66 (d, 30H, Cp^* -H).

Synthesis of complex **2**

A procedure analogous to the preparation of complex **1** was used: $[\text{Cp}^*\text{RhCl}_2]_2$ (62 mg, 0.1 mmol), **L1** (23.6 mg, 0.1 mmol) and AgOTf (51.2 mg, 0.2mmol) were added to THF (10 mL) and stirred for 12 h at

room temperature. Slow evaporation of a THF / diethyl ether solution of complex **2** in air produced red crystals suitable for X-ray crystallography. Yield: 111.4 mg (93%). Anal. Calcd (%) for $C_{35}H_{41}N_4O_{13}S_3F_9Rh_2$: C 35.07, H 3.45, N 4.67. Found: C 35.43, H 3.71, N 4.75. IR (KBr disk): 3421(w), 2345(w), 1718(w), 1607(s), 1490(s), 1382(s), 1318(w), 1264(s), 1082(w), 1026(s), 782(w), 752(m), 637(w) cm^{-1} . 1H NMR (400 MHz, CD_3OD , ppm): δ = 8.87-8.29 (d, 2H, Py-H), 8.36-8.34 (d, 2H, Py-H), 7.96-7.91 (d, 2H, Py-H), 7.53-7.49 (d, 2H, Py-H), 7.24-7.20 (d, 2H, Py-H) 1.67 (d, 30H, Cp^*-H).

Synthesis of complex **3**

Bpe (18.3 mg, 0.1 mmol) was stirred with $[Cp^*RhCl_2]_2$ (62 mg, 0.1 mmol) in dry MeOH (10 mL) for 4 h at room temperature. AgOTf (51.2 mg, 0.2 mmol) was then added to the solution and the reaction was stirred in the dark for 12 h. Subsequently, sodium acetate (8.2 mg, 0.1 mmol) was added to the mixture, and this was vigorously stirred for 8 h at room temperature. Crystallization from dichloromethane / diethyl ether provided complex **3**. Yield: 187.5 mg (83%). Anal. Calcd (%) for $C_{88}H_{92}N_4O_{18}S_4F_{12}Rh_4$: C 46.74, H 4.10, N 2.48. Found: C 46.94, H 4.48, N 2.71. IR (KBr disk): 3474(w), 3100(w), 1609(w), 1455(s), 1261(s), 1223(s), 1157(s), 1071(w), 1030(s), 821(w), 638(w), 573(m), 517(w) cm^{-1} . 1H NMR (400 MHz, CD_3OD , ppm): δ = 7.53-7.51 (d, 4H, Py-H), 7.10-7.08 (d, 2H, CH_2 -H), 7.08-7.01 (d, 2H, CH_2 -H), 7.00-6.99 (t, 4H, Py-H), 2.18-2.17 (t, 6H, CH_3 -H), 1.61 (s, 60H, Cp^*-H).

Synthesis of complex **4**

A mixture of $[Cp^*RhCl_2]_2$ (62 mg, 0.1 mmol) and bpy (16 mg, 0.1 mmol) was added to 10 mL of MeOH for 8 h. AgOTf (51.2 mg, 0.2 mmol) was then added to the solution and the reaction was stirred in the dark for 12 h. Pyrazine-2,3-dicarboxylic acid (18.6 mg, 0.1 mmol) was then added to the solution and it was stirred for 8 h. Crystallization from dichloromethane / diethyl ether provided complex **4**. Yield: 160.5 mg (84%). Anal. Calcd (%) for $C_{74}H_{80}F_6N_8O_{14}Rh_4S_2$: C 46.90, H 4.25, N 5.91. Found: C 46.53, H 4.01, N 5.65. IR (KBr disk): 3462(w), 1654(w), 1609(w), 1384(s), 1341(s), 1280(s), 1258(s),

1123(w), 1096(s), 1031(s), 639(w), 567(m), 589(w) cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , ppm): δ = 9.47-9.42 (d, 4H, Py-H), 8.64-8.57 (d, 8H, bpy -H), 8.98-8.06 (d, 8H, bpy -H), 1.67 (s, 60H, Cp^* -H).

Synthesis of complex 5

Bpe (18 mg, 0.1 mmol) was stirred with $[\text{Cp}^*\text{IrCl}_2]_2$ (62 mg, 0.1 mmol) in dry dichloromethane (15 mL) for 8 h at room temperature. The solution was then worked up according to the synthetic method of complexes **3** and **4**. AgOTf (51.2 mg, 0.2 mmol) was then added to the solution and the reaction was stirred in the dark for 12 h. 3-(2-pyridyl)acrylic acid (14.9 mg, 0.1 mmol) was then added into the solution and it was stirred for 8 h. Crystallization from dichloromethane / diethyl ether provided complex **5**. Yield: 154.6 mg (61.2%). Anal. Calcd (%) for $\text{C}_{81}\text{H}_{100}\text{N}_6\text{O}_{19}\text{NaIr}_4\text{S}_3\text{F}_9$: C 38.59, H 4.00, N 3.33. Found: C 38.86, H 4.21, N 3.61. IR (KBr disk): 3500(w), 3100(w), 2963(w), 1602(s), 1557(s), 1455(s), 1260(s), 1123(w), 1156(s), 1030(s), 801(w), 637(s), 572(s) cm^{-1} . ^1H NMR (400 MHz, CD_3OD , ppm): δ = 8.97-8.92 (d, 2H, Py-H), 8.34-8.31 (d, 2H, Py-H), 8.17-8.12 (d, 2H, Py-H), 7.85-7.79 (t, 2H, Py-H), 7.57-7.55 (t, 18H, bpy-H), 7.46-7.37 (t, 18H, bpy-H), 1.62 (d, 60H, Cp^* -H).

X-ray crystal structure determination

All determinations of unit cell data were performed with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) for complexes **1-5**. Data were collected at 173(2) K using the ω scan technique. These structures were solved by direct methods, using Fourier techniques, and refined on F^2 by a full-matrix least-squares method. All calculations were carried out with the SHELXTL [32] program. Crystal data, data collection parameters, and the results of the analysis of these complexes are listed in Table 1.

The crystallographic data of complexes **1-5** are summarized in Table 1. CCDC-1447454 (**1**), 1447455 (**2**), 960939 (**3**), 1447456 (**4**), 960940 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Table 1. Crystallographic data and structure refinement parameters for complexes **1-5**

	1	2	3	4	5
Chemical Formula	C ₃₈ H ₄₉ Ir ₂₆ O ₃	C ₃₅ H ₄₁ N ₄ O ₁₃ Rh ₂ S ₃ F ₉	C ₉₄ H ₉₄ N ₄ O ₁₈ Rh ₄ S ₄ F ₁₂	C ₇₆ H ₈₀ N ₈ O ₂₀ Rh ₄ S ₄ F ₁₂	C ₈₁ H ₁₀₀ N ₆ O ₁₉ NaIr ₄ S ₃ F ₉
FW	1092.55	1202.75	2403.03	2193.36	4601.6
T/[K]	173(2)	173(2)	173(2)	173(2)	173(2)
$\lambda/\text{\AA}$	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	P 21/c	P -1	C 2/c	C 2/m	P -1
a/ $\text{\AA}$	13.1340(16)	8.4908(7)	40.798(3)	17.808(4)	15.2581(10)
b/ $\text{\AA}$	14.3378(18)	13.2306(12)	12.7785(9)	30.496(7)	16.3033(11)
c/ $\text{\AA}$	20.753(3)	21.2880(18)	19.3259(14)	8.5731(19)	19.5833(13)
$\alpha/^\circ$	90	83.4130(10)	90	90	93.1680(10)
$\beta/^\circ$	95.890(2) $^\circ$	87.2760(10)	105.7910(10)	101.977(4) $^\circ$	103.1230(10)
$\gamma/^\circ$	90	77.3800(10)	90	90	102.6100(10)
V/ $\text{\AA}^3$	3887.5(8)	2317.7(3)	9695.1(12)	4554.4(18)	4601.6(5)
Z	4	2	4	2	2
F(000)	2120	1212	4840	2208	2456
Reflections collected	25399	16289	33427	15838	36018
Completeness to θ	99.8%	98.4%	99.4%	99.1%	98.5%
Data/restraints/param.	7966 / 2 / 462	9954/ 131 / 665	10404 / 92 / 556	5030 / 31 / 265	22563 / 89 / 1078
Goodness-of-fit on F^2	1.073	1.131	1.061	1.000	0.998
Final R indices [$I > 2\sigma(I)$]	R ₁ = 0.0324 wR ₂ = 0.0950	R ₁ = 0.0497 wR ₂ = 0.1475	R ₁ = 0.0598 wR ₂ = 0.1718	R ₁ = 0.0761 wR ₂ = 0.2113	R ₁ = 0.0541 wR ₂ = 0.1645
Largest diff. peak/ hole (e $\text{\AA}^{-3}$)	1.915/-1.875	2.177/-1.014	1.582/-1.205	1.857/-1.012	5.598/-2.097

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ (based on reflections with $F_o^2 > 2\sigma F^2$). $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (also with $F_o^2 > 2\sigma F^2$)

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Half-sandwich rhodium and iridium complexes were prepared and their electrochemical properties were studied. A flexible macrocycle substrate led to the existence of a 1D zigzag chain coordination polymer.