A New Anion Receptor Based on (Trisubstituted cyclopentadienyl)ruthenium(II) Complexes

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New cationic (trisubstituted cyclopentadienyl)(cymene)-ruthenium(II) complexes were prepared and shown to form host-guest complexes with various anions, providing the first examples of the anion receptors based on cationic ruthenium complexes.

The molecular recognition of anionic guest species by positively charged or electron-deficient neutral abiotic organic receptors is an area of current interest and several neutral and cationic synthetic molecules have been shown to form host-guest complexes with common anionic species.[1] During the last few years Beer *et al.* reported that the redox-active positively charged cobalticinium complexes are useful for anionic recognition.[2] We have also shown that planar-chiral cobalticinium complexes having a trisubstituted cyclopentadienyl ligand can recognize not only various anionic species but also the shape of guest molecules.[3] These results and an x-ray crystallographic study[4] of the host-guest complex, **1**•Tso$^-$ ([Cp'Cp*Co]$^+$•TsO$^-$), reveal that the hydrophobic cavity constructed by substituents on the cobalticinium complex is an important component for a successful anion recognition. (Figure 1a) As an extension of our research, here we report the first examples of anion receptors based on positively charged (trisubstituted cyclopentadienyl)ruthenium complexes. (Figure 1b) Cationic CpRu(arene) complexes bearing various substituents on the arene ligand are prepared by simple arene exchange reaction.[5, 6] The Ru complexes described here, compared with known cationic metallocene-type anion receptors, have a great advantage in easy construction of the binding site suitable for complexation with an anion.

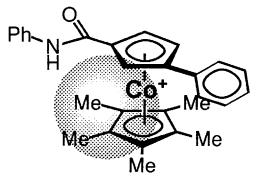

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Figure 1a.

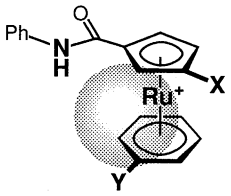
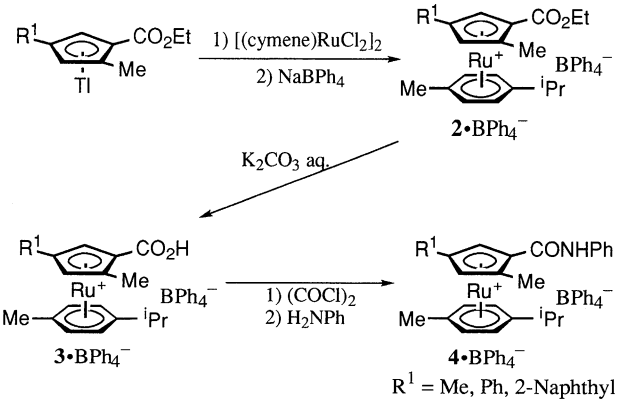


Figure 1b.

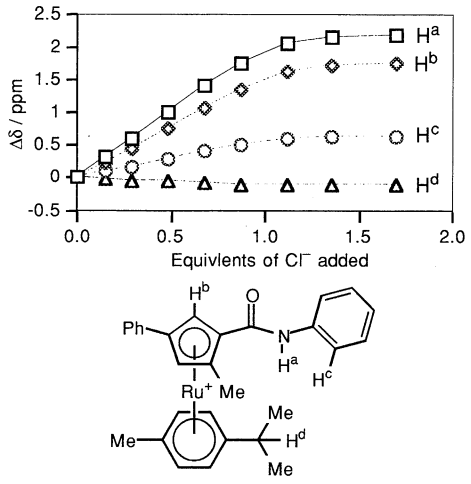
: ***Anion***

Such the anion receptors based on cationic Cp'(arene)Ru complexes were prepared as shown in Scheme 1. (Trisubstituted cyclopentadienyl)thallium, prepared from Cp^{1}H and thallium sulfate, was reacted with [(cymene)RuCl$_2$]$_2$ in acetonitrile.[6, 7] The crude product was treated with sodium tetraphenylborate followed by recrystallization from EtOH-CHCl$_3$ to give pure cationic Cp^{1}Ru(cymene) (**2**) as white to pale yellow crystalline solids in a moderate yield. The hydrolysis of ester derivative **2** under basic conditions gave carboxylate **3** in a good yield. Then **3** was converted into amide derivative **4** via acid chloride by a usual amidation method.



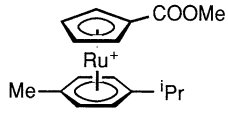
Scheme 1.

In order to investigate an ability of these new complexes as an anion receptor, we carried out ^{1}H NMR spectroscopic titration for **2** and **4**. In the titration studies, addition of tetraalkylammonium salt of Cl$^-$ into a deuterated acetone solution of **4b** resulted in remarkable shifts of the Cp-5H and amide-proton signal.



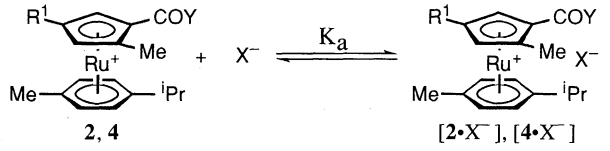
4b

Figure 2. ^{1}H NMR titration curve of **4b** and Cl$^-$ in acetone-d_6.



2d

Figure 3.



2, 4 [2•X⁻], [4•X⁻]

2: COY = COOEt, 4: COY = CONHPh
R^1 = Me, Ph, 2-Naphthyl

Scheme 2.

Table 1. Association constants (K_a) between Cp^1-Ru complexes and Anions

entry	Host	R^1	COY	Anion	K_a / M^{-1} [a]
1	**2a**	Me	COOEt	TsO^-	~ 0
2	**2b**	Ph	COOEt	TsO^-	2.9 x 10^2
3				Cl^-	3.0 x 10^2
4				I^-	1.5 x 10^2
5				AcO^-	2.8 x 10^2
6	**2c**	2-Naph[b]	COOEt	TsO^-	3.2 x 10^2
7	**2d**	H	COOMe	TsO^-	~ 0
8	**4a**	Me	CONHPh	TsO^-	4.3 x 10^3
9	**4b**	Ph	CONHPh	TsO^-	9.4 x 10^3
10				Cl^-	2.0 x 10^4
11				I^-	1.5 x 10^3
12				AcO^-	2.7 x 10^4
13				Camph-SO_3^- [c]	2.3 x 10^4
14	**4c**	2-Naph[b]	CONHPh	TsO^-	1.5 x 10^4

[a] solvent: acetone-d_6. [b] 2-Naph = 2-naphthyl. [c] Camph-SO_3^- = 10-camphorsulfonate.

The titration curves (Figure 2) indicate the formation of a host-guest complex ([**4**•X^-]) with a clear 1:1 stoichiometry in solution. (Scheme 2) On addition of about one equivalent of chloride anion, substantial shifts were obserbed for most of protons on **4b** (Cl^-/**4b** = 1.1; Δδ (ppm): H^a, 2.061; H^b, 1.619; H^c, 0.588; H^d, -0.114). Then association constants (K_a) between the Ru host complexes (**2** and **4**) and various inorganic and organic anions were estimated from the titration curves by a nonlinear curve fitting procedure[8] and are summarized in Table 1. In the titration studies of **2** and **4** with TsO^- (entries 1, 2, 6 and 7 for **2**; 8, 9 and 14 for **4**), the host complex having a larger hydrophobic substituent R^1 on the Cp^1 ligand showed a larger K_a. It is noteworthy that **2a** having a small R^1 of methyl group and simple monoester derivative **2d** (Figure 3) do not associate with TsO^- (Δδ ~0). As is the case with the cobalticinium host complexes,[3, 4] these results indicate that the hydrophobic cavity surrounded with anilide, R^1, and isopropyl groups on the Ru host complexes plays an important role in the anion recognition. The K_a's for **4** are greater than those for **2**. In addition large downfield shifts were observed for the amide-proton signals in the titration for **4**, implying that an intermolecular electrostatic interaction of the host Ru complex with a guest anion through a hydrogen bonding between amide proton and anion is an essential component for an anion binding process.

We can also observe an anion-selective recognition. The K_a's decrease in the order of $Cl^- > TsO^- > I^-$ for both **2b** and **4b** (entries 2, 3 and 4 for **2b**; 9, 10 and 11 for **4b**) In particular, the titration of **4b** with Cl^- gave a K_a of 2.0 x 10^4 M^{-1} which is about ten times as large as that for **4b** with I^- (1.5 x 10^3 M^{-1}).

To our knowledge, the cationic Cp'-Ru complexes described here provide the first examples of anion receptors based on ruthenium complexes, and can be expected to recognize various anions with a selectivity.

References and Notes

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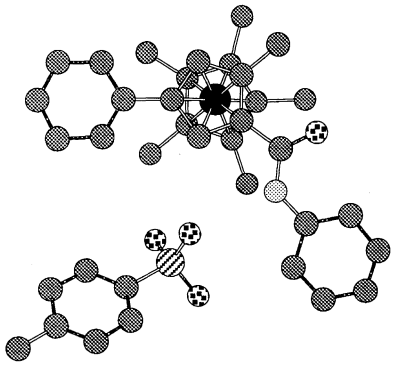
4 Crystal data for **1**•TsO^- ([Cp'Cp*Co]$^+$•TsO^-): $C_{36}H_{38}NO_4SCo$, M = 639.69, monoclinic, space groupe $P2_1/c$, a = 8.248(3), b = 17.351(5), c = 22.404(4) Å, β = 90.21(3), V = 3206 $Å^3$, Z = 4, D_C = 1.33 gcm^{-3}, Mo-Kα (graphite monochromated) radiation, μ(Mo-Kα) = 6.40 cm^{-1}. 9641 reflections were collected at 20 °C on a Rigaku AFC-5FOS four-circle diffractometer in the ω–2θ scan mode to $2\theta_{max}$ = 60°. The structure was solved by Patterson techniques and refined by full-matrix least squares to give R = 0.065, R_W = 0.074 for 3918 independent reflections [I > 3σ(I)].



Molecular structure (Top view) of **1**.
Hydrogen atoms have omitted for clarity.

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