# η5-FLUORENYL RHODIUM COMPLEXES: ARE THEY A MYTH OR REALITY?

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## Abstract

The synthesis of η5-fluorenyl rhodium complexes is challenging and poorly studied. In this work, we demonstrate that even a very bulky fluorene such as hexadecahydrotetrabenzo[*a,c,d,f*]fluorene does not form η5-fluorenyl derivatives. Only the rhodium complex with a η6-coordination mode was synthesized and analyzed by X-ray diffraction. DFT calculations also confirmed the low thermodynamic stability of the η5-fluorenyl rhodium complexes.

**Key words:** rhodium, cyclopentadienyl, fluorenyl, arene complexes.
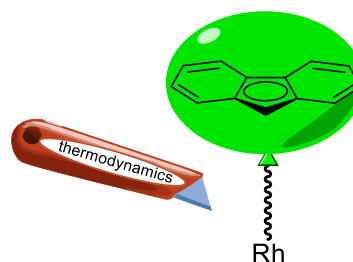
## Introduction

Organometallic catalysis is an important part of modern organic chemistry. Half-sandwich complexes of transition metals are conventional catalysts for a variety of processes such as hydrogenation of unsaturated bonds [1], oligomerization of olefins [2], C–H activation [3], *etc*. The cyclopentadienyl ligand usually acts as a cyclic moiety in the structure of these complexes and plays a role of a supporting ligand to stabilize the metal atom.

Along with cyclopentadiene, its benzannulated analogs, such as indene and indacene, can be used for the catalyst design, which was reviewed in detail earlier [4, 5]. The introduction of fused benzene rings into the ligand structure leads to an increase of its coordination lability. The most famous example of such phenomenon is "the indenyl effect", which is expressed in a manifold increase in the reactivity of indenyl complexes compared to cyclopentadienyl analogs [6]. The main reason for such behavior is an ability of indenyl ligands to change their coordination mode from η5 to η3, which leads to the appearance of a coordination vacancy on the metal atom and thereby facilitates substitution reactions and catalytic processes.

To date, the catalytic activity of indenyl, benzindenyl and indacenyl complexes has been well investigated [7–9], while the complexes of middle and late transition metals with a fluorenyl ligand have remained almost unexplored. The rare examples of η5-fluorenyl complexes are known for iron [10] and ruthenium [11]. There is also a communication devoted to the synthesis of the η5-fluorenyl rhodium(I) complex (η5-fluorenyl)Rh(cod) [12]. The authors demonstrated its high catalytic activity in the [2+2+2] cycloaddition, but did not provide evidence of its structure. On the other hand, several examples of stable η5-fluorenyl cobalt complexes are known [13]. This inspired us to investigate the possibility of obtaining η5-fluorenyl rhodium complexes for subsequent use in homogeneous catalysis.

## Results and discussion

First of all, we tried to accomplish the synthesis of (η5-fluorenyl)Rh(cod). This complex was previously reported by Ingrosso and Lucherini with co-workers without the experimental details [12]. However, the reaction of lithium fluorenide with [(cod)RhCl]2 in our hands led only to the formation of a mixture of unidentified products. The use of [(cod)IrCl]2 instead of the rhodium derivative also did not give the desired product with a η5-coordinated fluorenyl ligand. Nevertheless, Macgregor and Mansell, when conducting a similar reaction with [(coe)2RhCl]2, detected the formation of (η5-fluorenyl)Rh(COE)2 by NMR spectroscopy [14]. The authors noted the low stability of this compound, the impossibility of its purification, and the side formation of large amounts of metallic rhodium as a result of the elimination of the fluorenyl ligand.

It is well known that the introduction of alkyl substituents into the supporting ligand leads to stabilization of its bond with the metal atom [15, 16]. According to this tendency, to overcome the low stability of η5-fluorenyl rhodium complexes, we tried to use highly substituted hexadecahydrotetrabenzo[*a,c,d,f*]fluorene, which was synthesized by the published procedure [17]. Unfortunately, the reactions of its lithium derivative with [(cod)RhCl]2 or [(C2H4)2RhCl]2 also did not yield isolable target products (Scheme 1). An attempt to use the 9-trimethylsilylfluorenide anion, which contains an additional bulky substituent directly in the five-membered ring, as a fluorenyl ligand source was also unsuccessful.

Nevertheless, we succeeded in synthesizing rhodium complex **1**(SbF6)2, containing η6-coordinated hexadecahydrotetrabenzo[*a,c,d,f*]fluorene, using the reaction with [CpRhI2]n in the presence of AgSbF6 (Scheme 2). The yield was 63%. This suggests that our previous failures in preparing
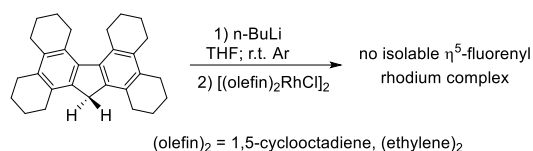
**Scheme 1.** Attempts to synthesize $\eta^5$-fluorenyl rhodium complexes based on hexadecahydrotetrabenzo[*a,c,d,f*]fluorene.

$\eta^5$-fluorenyl rhodium complexes are most likely not due to the steric factors. However, it should be noted that the steric factor still cannot be completely ignored, since along with **1**(SbF$_6$)$_2$, about 15% of [Cp$_2$Rh]SbF$_6$ also formed according to the NMR data. Moreover, we failed to synthesize the related complex with a bulkier Cp*Rh moiety using [Cp*RhCl$_2$]$_2$ instead of [CpRhI$_2$]$_n$ as the starting compound. The structure of complex **1**(SbF$_6$)$_2$ was determined by XRD (Fig. 1).



**Scheme 2.** Synthesis of arene complex **1**(SbF$_6$)$_2$ with hexadecahydrotetrabenzo[*a,c,d,f*]fluorene.
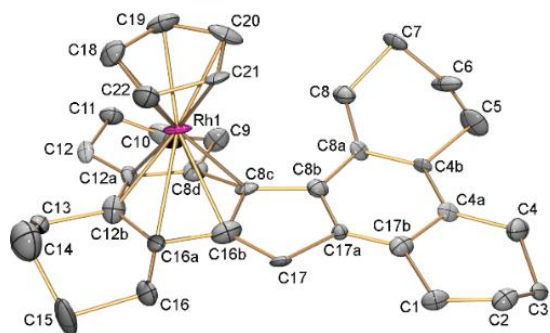


**Figure 1.** Molecular structure of cation **1** with atoms shown as thermal ellipsoids at 50% probability level. The hydrogen atoms are omitted.

In order to explain the low stability of $\eta^5$-fluorenyl rhodium complexes, we performed the DFT calculations for replacement of Cp, $\eta^5$-indenyl, and $\eta^5$-fluorenyl ligands by water in complexes [Cp$_2$Rh]$^+$, [CpRh($\eta^5$-indenyl)]$^+$, and [CpRh($\eta^5$-fluorenyl)]$^+$ (Scheme 3). The addition of two water molecules is accompanied by the hapticity change of the fluorenyl ligand from $\eta^5$ to $\eta^1$. It was found that, in the case of the cyclopentadienyl and indenyl derivatives, this process is *ca.* 26 and 13 kcal·mol$^{-1}$ endergonic, respectively. In contrast, the replacement of the fluorenyl ligand is 1.6 kcal·mol$^{-1}$ exergonic, which explains the low stability of $\eta^5$-fluorenyl rhodium complexes (for the details, see the Electronic supplementary information (ESI)).
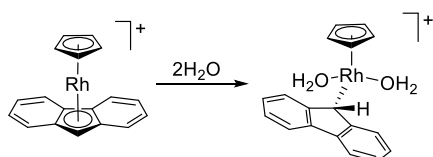


**Scheme 3.** Substitution of the fluorenyl ligand by water.

## Conclusions

In summary, based on the analysis of the literature data as well as our experimental and theoretical data, we can conclude that although the $\eta^5$-fluorenyl rhodium complexes can be detected in reaction mixtures, they are unstable compounds due to the high lability of the fluorenyl ligand. Therefore, the use of the fluorene derivatives as the supporting ligands in catalysis seems unlikely.

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## Electronic supplementary information

Electronic supplementary information (ESI) available online: the experimental details, NMR spectra for the compound obtained, and atomic coordinates for the optimized geometries. For ESI, see DOI: 10.32931/io2510a.

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