

Review

Cyclopentadienyl ruthenium complexes with naphthalene and other polycyclic aromatic ligands



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ARTICLE INFO

Article history:

Received 8 March 2014

Accepted 19 June 2014

Available online 27 June 2014

Keywords:

Ruthenium

Naphthalene

Polyarene

Cyclopentadienyl

Ligand exchange

Catalysis

ABSTRACT

Synthesis, reactivity and application of cyclopentadienyl ruthenium complexes with naphthalene and other polycyclic aromatic ligands (polyarenes) are reviewed. The parent naphthalene complex [CpRu(C₁₀H₈)]⁺ is readily obtained from ruthenocene while its substituted analog [Cp^{*}Ru(C₁₀H₈)]⁺ is prepared by direct reaction of RuCl₃·xH₂O with Cp^{*}H and C₁₀H₈. More sophisticated polyarene complexes including binuclear species are synthesized from the half-sandwich precursors [Cp^{*}RuCl₂]₂, [Cp^{*}RuCl]₄, and [(C₅R₅)Ru(MeCN)₃]⁺. Coordinated naphthalene in [CpRu(C₁₀H₈)]⁺ can be exchanged for various 2-electron ligands under thermal or photochemical conditions giving half-sandwich complexes CpRuL₂X and [CpRuL₃]⁺ (L = phosphines, N-heterocycles, dienes; X = Cl, Br, I, N₃). Similar reactions of [CpRu(C₁₀H₈)]⁺ with cyclopentadienes or arenes produce sandwich compounds CpRu(C₅R₅) or [CpRu(arene)]⁺, respectively. The ability of [CpRu(C₁₀H₈)]⁺ to generate the catalytically active species [CpRuL_x]⁺ can be used to promote anti-Markovnikov hydration and cyclotrimerization of alkynes, as well as for

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enantioselective Carroll rearrangement. In overall it can be concluded that stable and easily accessible $[(C_5R_5)Ru(\text{polyarene})]^+$ complexes represent convenient precursors for organometallic synthesis and catalysis.

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1. Introduction

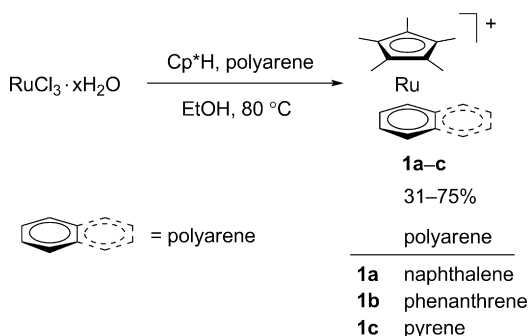
Transition metal complexes with polycyclic aromatic ligands (polyarenes) are interesting from several points of view. First, they provoke fundamental questions of how many metals can coordinate one polyarene and which ring of a polyarene is preferred for coordination. Second, many polyarenes have peculiar photochemical and electrochemical properties [1] and metal coordination can be used to modify them. Finally, polyarene complexes readily exchange ligands and therefore can be used as convenient precursors in organometallic synthesis and catalysis [2–5].

The cyclopentadienyl ruthenium cation $[CpRu]^+$ forms exceptionally stable arene complexes $[CpRu(\text{arene})]^+$. This makes it useful for the synthesis of polyarene complexes, which are generally more labile than their benzene congeners. Practical interest in ruthenium polyarene complexes arise from their potential application in catalysis and biochemistry. In this review we have tried to cover all available literature on the cyclopentadienyl ruthenium complexes with polyarene ligands, which is indexed by Web of knowledge, Reaxys, and Cambridge Crystallographic Database by the end of 2013.

2. Synthesis of polyarene complexes

2.1. Direct synthesis from $RuCl_3$

Direct reaction of $RuCl_3 \cdot xH_2O$ with Cp^*H and two equivalents of naphthalene, phenanthrene or pyrene in refluxing ethanol gives complexes $[Cp^*Ru(\text{polyarene})]^+$ (**1a–c**) in 31–75% yield [6] (Scheme 1). This method was originally proposed by our group [7] for preparation of the benzene complex $[Cp^*Ru(C_6H_6)]^+$ and then successfully applied to functionalized arenes by Lindel et al. [8]. The choice of the solvent is important because ethanol not only provides sufficient solubility for both polar and nonpolar reactants but also acts as a gentle reducing agent converting the Ru^{III} salt into a Ru^{II} complex. Although this method is the most straightforward, it is currently limited to the synthesis of complexes with Cp^* ligand. Heating of less substituted cyclopentadienes with $RuCl_3 \cdot xH_2O$ may result in formation of Diels–Alder dimers as well as ruthenocenes [9]. However, the method may be successful in the case of bulky cyclopentadienyl ligands which give stable intermediate complexes $[(C_5R_5)RuCl_2]_2$ [10–12].



Scheme 1. Synthesis of polyarene complexes from $RuCl_3 \cdot xH_2O$ [6].

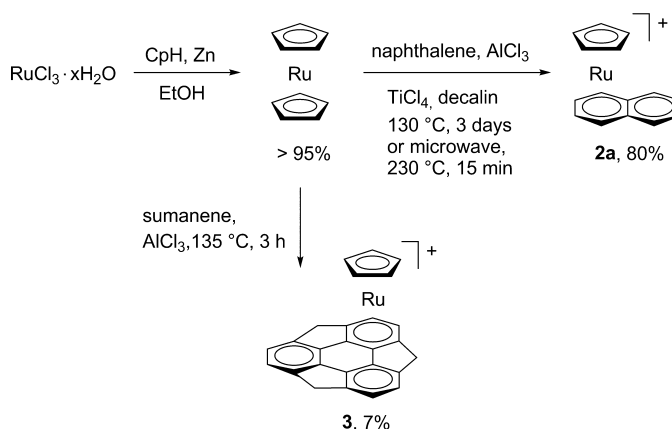
2.2. Synthesis via Cp_2Ru

Ferrocene reacts with various arenes at 70–100 °C in the presence of $AlCl_3$ and aluminum powder, giving the corresponding arene complexes $[CpFe(\text{arene})]^+$ in good yield [13,14]. Ruthenocene is more robust than ferrocene and therefore similar reaction requires higher temperature and produces $[CpRu(\text{arene})]^+$ complexes in lower yields [15,16]. In particular, heating of Cp_2Ru with naphthalene at 130 °C gives complex $[CpRu(C_{10}H_8)]^+$ (**2a**) in only 13% yield [17] (Scheme 2). However, Kündig and Monnier have found that the yield of **2a** can be increased up to 80% by addition of $TiCl_4$, which traps liberated cyclopentadiene in the form of titanocene dichloride [18]. Furthermore, the reaction time can be reduced from 3 days to 15 min by conducting the synthesis at 230 °C using microwave irradiation [19].

The starting material Cp_2Ru is easily prepared from $RuCl_3 \cdot xH_2O$ and cyclopentadiene in almost quantitative yield [17,18]. However, drastic conditions of its further reaction with polyarene prevent wide application of this method. Most functional groups are incompatible with $AlCl_3$ and hydrogenation of some polyarenes can also occur [20,21]. Apart from **2a**, the only polyarene complex prepared so far by this procedure is the cation $[CpRu(\text{sumanene})]^+$ (**3**) [22]. This compound exhibits interesting dynamic behavior in solution, namely inversion of the sumanene bowl.

2.3. Synthesis via Cp^*Ru chlorides or methoxide

In 1984 Japan [23] and USA [24] scientists independently reported that heating of $RuCl_3 \cdot xH_2O$ with Cp^*H produces dimeric Ru^{III} chloride $[Cp^*RuCl_2]_2$ (**4**) (Scheme 3). This compound was later reduced to give Ru^{II} chloride $[Cp^*RuCl]_4$ (**5**) [25] or methoxide $[Cp^*RuOMe]_2$ (**6**) [26] (see Schemes 4 and 5). Chloride **4** reacts with benzene in refluxing ethanol in the presence of silver salts to give the corresponding complex $[Cp^*Ru(\text{benzene})]^+$ [27,28]. Roman et al. [29] have used this method for the preparation of various polyarene complexes **1a–f** in 40–80% yields. Interestingly the first transition metal complex with coronene **1g** was also obtained this way, albeit in only 10% yield. The reactions of phenanthrene and chrysene with 2-fold excess of **4** gave the dinuclear complexes



Scheme 2. Synthesis of polyarene complexes via Cp_2Ru [18].

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