

Review

Cyclobutadiene complexes of platinum metals[☆]Nikita V. Shvydkiy, Dmitry S. Perekalin^{*}

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ABSTRACT

Synthesis and reactivity of the cyclobutadiene complexes of platinum metals are reviewed. Palladium and platinum complexes are well developed and are mainly represented by the half-sandwich compounds such as $(C_4R_4)PtCl_2$ and their adducts. On the other hand, ruthenium and rhodium complexes have been studied only fragmentarily and are mainly represented by the sandwich compounds such as $Cp^*Ru(C_4R_4)X$ and $Cp^*Rh(C_4R_4)$. Most of the complexes are synthesized via dimerization of internal alkynes by unsaturated metal precursors, although this method often suffers from the side oligomerization of alkynes. Once formed, the cyclobutadiene ligand typically remains intact even under rather harsh conditions, which makes it a promising protecting ligand for metal catalysts.

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1. Introduction

Platinum metal complexes are widely used as catalysts. These complexes are usually equipped with phosphine ligands, which help to stabilize the active metal center and control the selectivity of reactions. Diene, cyclopentadienyl and arene ligands are also often used for these purposes, especially in the case of ruthenium and rhodium complexes (see, for example, some recent reviews [1–3]). At the same time, to the best of our knowledge, there were no reports on successful application of the cyclobutadiene complexes in catalysis prior to 2016 [4,5]. This is partially because of

their more complicated synthesis, which stems from instability of the cyclobutadiene as a free ligand.

Cyclobutadiene itself is anti-aromatic, but as many other molecules it can be stabilized by coordination with transition metals. In terms of valence electron count it provides metal 4 electrons like other dienes. It is sometimes assumed that upon coordination the cyclobutadiene accepts two electrons from the metal in order to reach the aromatic sextet. However, the calculated charge distribution is far from this polarized picture and the metal-cyclobutadiene bond is mostly covalent [6]. From the structural point of view, cyclobutadiene almost exclusively binds metals symmetrically in η^4 -fashion (rare exceptions are the compounds **36** and **38** in this review). Coordinated cyclobutadiene is typically a square with an average C–C distance of 1.46 Å, which is much closer to C_{sp^2} – C_{sp^2} single bond length (1.45 Å) rather than to C=C double bond length (1.34 Å) of butadiene [7] (Fig. 1).

[☆] Dedicated to Prof. Peter M. Maitlis in recognition of his fundamental contribution to the chemistry of the cyclobutadiene complexes and on the occasion of his 85th birthday.

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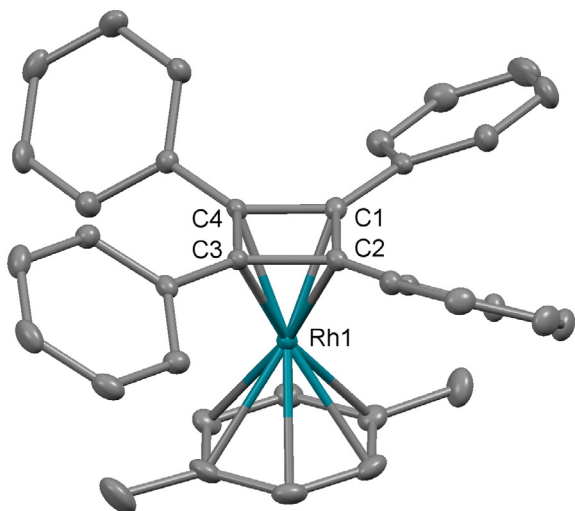


Fig. 1. An example of the crystal structure of the cyclobutadiene complex, namely $[(C_4Ph_4)Rh(p\text{-xylene})]PF_6$ [8]. The PF_6^- anion and the hydrogen atoms are omitted for clarity. Selected distances (Å): Rh1–C1 2.115(2), Rh1–C2 2.113(2), Rh1–C3 2.120(2), Rh1–C4 2.116(2), C1–C4 1.464(3), C1–C2 1.469(3), C2–C3 1.464(3), C3–C4 1.464(3).

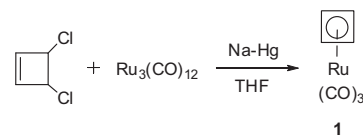
The most common method for the synthesis of the cyclobutadiene complexes of platinum metals is the dimerization of alkynes in the coordination sphere of the metal. However, this method suffers from the inherent high reactivity of alkynes, which often leads to formation of oligomerization products. The reactions of metal precursors with alkynes have been widely studied and a vast number of unusual and apparently unrelated molecules have been isolated [9]. In many cases it is difficult to rationalize the factors affecting the reaction and predict the structure of products.

Recently we have developed a new general method for synthesis of cyclobutadiene rhodium complexes from alkynes [8,10] and demonstrated their application as catalysts for reductive amination [4]. We hope that the availability of these cyclobutadiene complexes will awaken the general interest and will lead to wide investigation of this class of organometallic catalysts.

This review summarizes the available information on synthesis and properties of the cyclobutadiene complexes of platinum metals, which is indexed by Reaxys and Web of Knowledge databases by the end of 2016. The discussion is organized according to periodic table of elements – from ruthenium to platinum. To the best of our knowledge, the cyclobutadiene complexes of osmium remain unknown and only one iridium complex has been reported [10]. The only comprehensive review on transition metal complexes with cyclobutadiene ligands was published in 1977 [11]. A personal view on the chemistry of the cyclobutadiene palladium complexes was published by Prof. P.M. Maitlis in 1980 [12]. A more recent review was also published [13], but it has very limited availability. The intriguing history of prediction and synthesis of the cyclobutadiene complexes is described in the essay by Prof. D. Seyferth [14].

2. Ruthenium complexes

Cyclobutadiene complexes of ruthenium have been studied in a bit unsystematic manner because general convenient methods for their synthesis are still unknown. Historically such compounds were first prepared by reactions of ruthenium carbonyls with precursors having pre-organized C_4 -cycle. For example, the complex with unsubstituted cyclobutadiene $(C_4H_4)Ru(CO)_3$ (**1**) was prepared from 3,4-dichlorocyclobutene in a low yield [15] (Scheme 1).



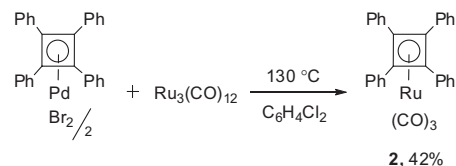
Scheme 1. Synthesis of ruthenium complex with unsubstituted cyclobutadiene [15].

Analogous tetraphenyl-substituted complex $(C_4Ph_4)Ru(CO)_3$ (**2**) was obtained by ligand transfer reaction from palladium complex $[(C_4Ph_4)PdBr_2]_2$ at 130 °C [16,17] (Scheme 2). This method was later extended for preparation of the ruthenium cluster complexes $(C_4Ph_4)Ru_5C(CO)_{13}$ and $(C_4Ph_4)Ru_6C(CO)_{15}$ [18,19]. In this case the more labile precursor $[(C_4Ph_4)Pd(Me_2CO)_3][BF_4]_2$ was used, which transfers cyclobutadiene ligand even at the room temperature.

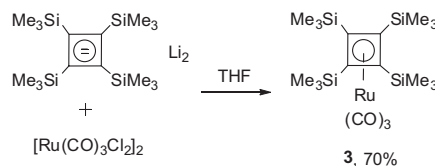
Reduction of the cyclobutadiene cobalt complex $((Me_3Si)_4C_4)CoCp$ produces the lithium salt of the cyclobutadiene dianion $Li_2[C_4(SiMe_3)_4]$ [20,21], which reacts with $[Ru(CO)_3Cl_2]_2$ giving the corresponding complex $((Me_3Si)_4C_4)Ru(CO)_3$ (**3**) in good yield [22] (Scheme 3). Interestingly, complexes with tetrasilylcyclobutadiene and tetragermanacyclobutadiene [23] can be also prepared in a similar way.

However, the dominant strategy for the synthesis of the cyclobutadiene ruthenium complexes is a dimerization of two alkynes in the coordination sphere of the metal. The common mechanism for this process includes the sequential π -coordination of alkynes [24], the formal “oxidative insertion” with formation of the intermediate metallacycle $Cp^*Ru^{IV}(\eta^1, \eta^1-C_4R_4)Cl$ (**4**) and the formal “reductive elimination” giving the cyclobutadiene complex $Cp^*Ru^{II}(\eta^4-C_4R_4)Cl$ [25] (Scheme 4). According to the DFT calculations, the rate limiting step is the reductive elimination which has an activation energy of 25–40 kcal mol⁻¹.

Experimentally, the best results are obtained for the alkynes with bulky aromatic or Me_3Si substituents, presumably because these groups block the alternative transformations of alkynes (e.g. cyclotrimerization). Besides, DFT calculations predict that Me_3Si groups increase the thermodynamic stability of the substituted cyclobutadiene complex compared to isomeric metallacycle [25]. The chloride $[Cp^*RuCl]_4$ reacts with $Me_3SiC\equiv CH$ or $Me_3SiC\equiv CCO_2Et$ to give the corresponding cyclobutadiene complexes **5** [26,27] (Scheme 5). Similar reaction of $Cp^*Ru(tmeda)Cl$ (**6**; tmeda = tetramethylethylenediamine) with $Me_3SiC\equiv CH$ produces the cyclobutadiene complex **7** in which two bulky Me_3Si -groups are in vicinal positions [28]. The structure of **7** was unambiguously determined by the X-ray diffraction analysis, while the positions of substituents in the cyclobutadiene ligands of **5** were assigned only by NMR and therefore are not fully certain.



Scheme 2. Transfer of cyclobutadiene ligand from palladium to ruthenium [17].



Scheme 3. Synthesis from cyclobutadiene dianion [22].

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