Journal of Organometallic Chemistry 737 (2013) 21–25

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Reactions of the cyclopentadienyl ruthenium complexes $(C_5R_5)Ru(cod)Cl$ and $[(C_5R_5)Ru(MeCN)_3]^+$ (R = H, Me) with phenylacetylene and acetic acid: Unexpected difference in reactivity of CpRu and Cp*Ru complexes

Dmitry S. Perekalin, Evgeniya A. Trifonova, Valentin V. Novikov, Yulia V. Nelyubina, Alexander R. Kudinov*

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova str. 28, 119991 Moscow, Russian Federation

ARTICLE INFO

Article history:
Received 8 February 2013
Received in revised form
26 March 2013
Accepted 28 March 2013

Keywords:
Ruthenium
Cyclopentadienyl
Catalysis
Alkynes
Bridging ligand
Flyover ligand

ABSTRACT

Reaction of CpRu(cod)Cl with phenylacetylene and AcOH gives an unusual binuclear ruthenium complex $CpRu(\mu\text{-}\sigma,\eta^3:\eta^3,\sigma\text{-}C_6H_3Ph_3)RuCp$ (**5**, 58% yield) with a bridging acyclic flyover ligand $C_6H_3Ph_3$. Under similar conditions $[CpRu(MeCN)_3]^+$ undergoes an unexpected cleavage of Cp ligand giving 4,7-diphenyl-3a,7a-dihydroindene (**6**, 65% yield). In sharp contrast, the pentamethylated congeners Cp*Ru(cod)Cl and $[Cp^*Ru(MeCN)_3]^+$ react with phenylacetylene and AcOH in catalytic fashion giving 1,4-diphenyl-1-acetoxy-1,3-butadiene. The structures of **5** and **6** were established by X-ray diffraction. The mechanism of Cp ligand cleavage was proposed on the basis of DFT calculations.

1. Introduction

Cyclopentadienyl ruthenium complexes $(C_5R_5)Ru(cod)Cl$ (R = H (**1a**), Me (**1b**), cod = 1,5-cyclooctadiene; Chart 1) and $[(C_5R_5)Ru(MeCN)_3]^+$ (R = H (**2a**), Me (**2b**)) are widely used in organic synthesis as catalysts for various transformation of alkynes [1]. In catalytic reactions, labile cyclooctadiene and acetonitrile ligands are replaced by alkynes while cyclopentadienyl ligand remains intact thus stabilizing active ruthenium center. The catalytic behavior of complexes with Cp and Cp* ligands is considered to be similar, although the activity and selectivity of the unsubstituted congeners are sometimes diminished [2]. Herein we report the reactions of **1a** and **2a** with phenylacetylene and AcOH which are strikingly different from the analogous reactions of the pentamethylated congeners **1b** and **2b**.

2. Results and discussion

2.1. Synthesis and X-ray structures

In 2003, Dixneuf et al. have reported [3] that the cyclooctadiene complex **1b** catalyzes coupling of phenylacetylene with addition of acetic acid giving 1,4-diphenyl-1-acetoxy-1,3-butadiene (**3**) (Scheme 1). The reaction was shown to proceed via intermediate formation of ruthenacycle $Cp^*Ru(C_4H_2Ph_2)Cl$ (**4b**). We found that similar reaction of the unsubstituted complex **1a** gives only a small amount of **3** (11% yield). The major product is the unusual binuclear ruthenium complex $CpRu(\mu\text{-}\sigma,\eta^3:\eta^3,\sigma\text{-}C_6H_3Ph_3)RuCp$ (**5**) with a bridging flyover ligand $C_6H_3Ph_3$; it was isolated in 58% yield based on **1a**. The reaction of **1a** with phenylacetylene in the absence of AcOH also gives **5** albeit in a lower yield (27%). Although the mechanism of these reactions is unclear, one can assume that **1a** is first converted into ruthenacycle $CpRu(C_4H_2Ph_2)Cl$ (**4a**) as reported by Singleton et al. [4]. Intermediate **4a** is less electron rich than its Cp* congener **4b** and therefore it is not protonated by AcOH to give **3**. On the other hand, **4a** is less hindered than **4b**, explaining its further reaction with the second [CpRu] fragment and phenylacetylene to give **5**.

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* Corresponding author. Tel.: +7 499 135 9367; fax: +7 499 135 5085.
E-mail address: arkudinov@ineos.ac.ru (A.R. Kudinov).

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http://dx.doi.org/10.1016/j.jorganchem.2013.03.043

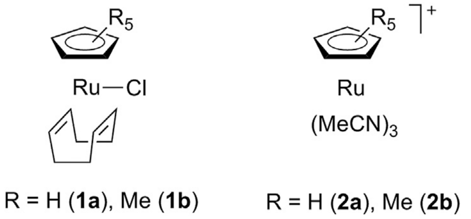


Chart 1. Catalytically active complexes **1a**,**b** and **2a**,**b**.

A few examples of complexes with bridging flyover ligands analogous to **5** were reported previously [5]. In particular, the cobalt complexes $(OC)_2Co(\mu\text{-}\sigma,\eta^3:\eta^3,\sigma\text{-}C_6R_6)Co(CO)_2$ were isolated as by-products of catalytic cyclotrimerization of alkynes in the presence of $Co_2(CO)_8$ [6]. However, despite the intensive studies of reactions of the cyclopentadienyl ruthenium complexes with alkynes [1,7], the formation of **5** was not described earlier. The only similar ruthenium flyover complex $CpRu(\mu\text{-}\sigma,\eta^3:\eta^3,\sigma\text{-}C_6Ph_2(COOMe)_4)RuCp$ was accidentally obtained by substitution of the carbonyl ligand in $CpRu(\mu\text{-}CO)(\mu\text{-}C_2Ph_2)RuCp$ with dimethyl acetylenedicarboxylate [8].

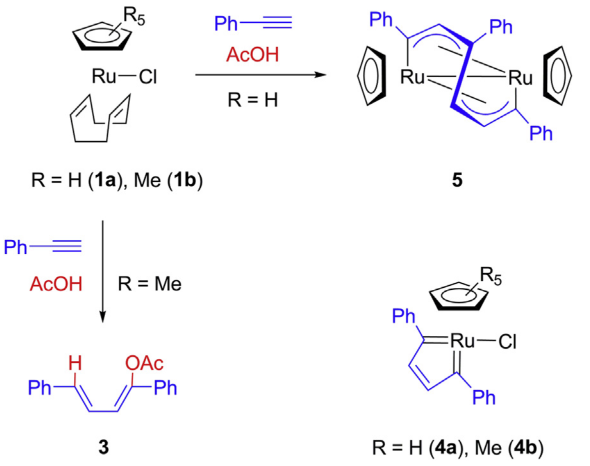
The reaction of the acetonitrile complex **2a** with phenylacetylene and AcOH in THF also gives **5** (38% yield) [9]. However, the same reaction in acetonitrile affords dihydroindene derivative **6** (65% yield) as a result of an unusual cleavage of Cp ligand (Scheme 2). The positions of phenyl substituents in **6** suggest that it is formed via decomposition of the tentative metallacycle **7**. Apparently strong coordinating ability of acetonitrile solvent facilitates the displacement of Cp ligand from **7** to give **6** (*vide infra*). Noteworthy the Cp cleavage occurs at room temperature. To the best of our knowledge similar process has been previously observed only for cyclopentadienyl-carboranyl ruthenium complexes and titanocenes [10]. As expected, Cp* ligand is not cleaved under similar conditions: the reaction of phenylacetylene and AcOH in the presence of **2b** in acetonitrile produces **3** in 69% yield (cf. 90% in the case of **1b** [3]).

The structures of compounds **5** and **6** were unambiguously established by the X-ray diffraction analysis (Figs. 1 and 2). The overall geometry of complex **5** is consistent with the proposed $\sigma,\eta^3:\eta^3,\sigma$-coordination of flyover bridging ligand $C_6H_3Ph_3$ (Scheme 1). In particular, C3–C4 distance (1.497 Å) is typical for $C(sp^2)$–$C(sp^2)$ single bond while C1–C2, C2–C3, C4–C5, and C5–C6 bonds (av. 1.425 Å) have significant double bond character. The Ru1–C1 and Ru2–C6 σ-bonds (av. 2.073 Å) are shorter than Ru1–C6 and Ru2–C1 π-bonds (av. 2.120 Å). The Ru1–Ru2 distance 2.728 Å qualifies for a single bond, which is required by 18-electron rule. The overall geometry of dihydroindene derivative **6** is unremarkable except for the C3A–C7A bond (1.570 Å) which is elongated due to the ring strain.

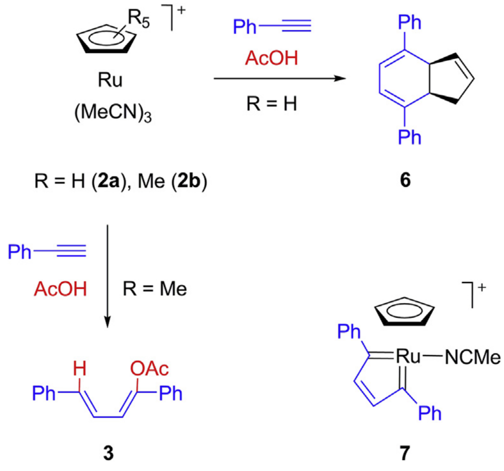
2.2. Calculated mechanism of the Cp ligand cleavage

We have evaluated a possible mechanism of Cp ligand cleavage in **2a** using relativistic DFT calculations at the PBE/L1 level (Fig. 3). The first step is a simple substitution of two MeCN ligands in **2a** by phenylacetylene molecules to give **8**; this step proceeds via a dissociative mechanism as established by experimental kinetic studies [11]. Further coupling of two alkynes to give metallacycle **7** proceeds via transition state **TS1** with a low activation barrier of 8.6 kcal mol^{-1} (Gibbs energies at 298 K are given). This is similar to 10.0 kcal mol^{-1} barrier calculated by Kirchner et al. for the formation of similar metallacycle $[CpRu(C_4H_4)(MeCN)]^+$ from **2a** and acetylene [9]. Subsequent addition of MeCN ligand to **7** has a higher barrier of 14.7 kcal mol^{-1} (**TS2**) due to the negative entropy contribution. The incoming MeCN ligand adds two electrons to the ruthenium center, transforming the Ru═C double bonds in **7** into more labile Ru–C single bonds in intermediate **IM1**. This promotes subsequent migration of one vinyl carbon atom to the Cp ring via transition state **TS3** (barrier 10.8 kcal mol^{-1}) giving intermediate **IM2** with η^4-coordination of the cyclopentadiene ligand. It should be noted that the change of coordination mode of Cp ligand was previously suggested as an important step of some catalytic reactions [12]. However, it generally does not lead to the cleavage of Cp ligand, which is observed in this case.

The addition of another MeCN ligand to **IM2** giving **IM3** presumably has a negligible barrier which we could not locate using various transition state search techniques. Note that this addition is favorable by 4.7 kcal mol^{-1} despite the negative entropy contribution. Again the incoming MeCN converts Ru═C bond in **IM2** into Ru–C bond in **IM3**. The cleavage of this bond via **TS4** (barrier 9.6 kcal mol^{-1}) gives complex **9**. On the further stages the η^2,η^3-dihydroindenyl ligand in **9** is apparently protonated by AcOH and then replaced by additional MeCN ligands giving **6**. Generally similar mechanism was recently calculated for Cp ring transformation in cyclopentadienyl-carboranyl ruthenium complexes [10c].



Scheme 1. The reactions of the cyclooctadiene complexes **1a**,**b** with phenylacetylene and AcOH.



Scheme 2. The reactions of the acetonitrile complexes **2a**,**b** with phenylacetylene and AcOH.