USE OF PHENYL-SUBSTITUTED CYCLOPENTADIENYL RHODIUM COMPLEXES IN THE C–H ACTIVATION

V. B. Kharitonov, Yu. V. Nelyubina, and D. A. Loginov*

Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, str. 1, Moscow, 119334 Russia

Abstract

Rhodium complexes with phenyl-substituted cyclopentadienyl ligands often remain underestimated in the study of C–H bond activation reactions due to their low catalytic efficiency. In this work, we demonstrate that the low catalytic efficiency is due to the low solubility of these complexes and can be significantly improved by using silver salts as additives. A protocol for the annulation of 4-methyl-*N*-(pivaloyloxy)benzamide with norbornene catalyzed by rhodium complexes with di- and triphenyl-substituted cyclopentadienyl ligands is developed.

**Key words:** rhodium, cyclopentadienyl, C–H activation.

Introduction

Cyclopentadienyl anion is one of the most popular ligands in modern organometallic chemistry. Since the discovery of its first complex, namely, ferrocene, an avalanche-like increase in the investigations devoted to organometallic chemistry and, in particular, cyclopentadienyl complexes began. According to the SciFinder database, a large library of cyclopentadienes is currently known, numbering about nine thousand derivatives. About 300000 complexes with metals and metalloids have been synthesized on their basis.

Aryl-substituted cyclopentadienes are of special interest for organometallic chemistry. Although the phenyl substituent is inferior to many functional groups as an inductive acceptor or as a mesomeric donor, as well as inferior to many fragments in terms of bulkiness, its high stability and ease of functionalization and inclusion into the cyclopentadiene framework make the phenyl-substituted Cp ligands rather popular. To date, there are about 3000 cyclopentadienes, containing at least one aryl substituent, and about 500 complexes based on them.

One of the main applications of polyarylcyclopentadienes is the kinetic stabilization of unstable complexes [1–4], including lanthanide derivatives [5]. Besides fundamental aspects, it was found that the lanthanide complexes with phenyl-substituted Cp ligands exhibit high activity in polymerization reactions [6] as well as extraordinary luminescent properties [7, 8]. In the latter case, a π-system of the aryl unit serves as an antenna for light, transferring energy to the metal ion.

In chemistry of transition metals, aryl-substituted Cp ligands are widely used for the design of homogeneous catalysts. In particular, they are implemented in the rhodium [9] and ruthenium-based hydrogenation catalysts, for example, the Shvo
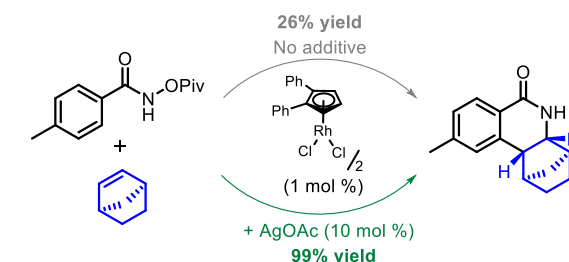
catalyst [10]. It is worth mentioning the complex (C₅Ph₅)Ru(CO)₂Cl—a commercially available catalyst used for the racemization of secondary alcohols [11].
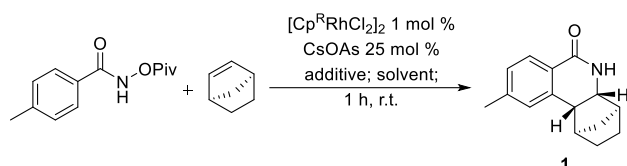
Besides the catalytic chemistry of noble metals, aryl-substituted Cp ligands are also represented among polymerization catalysts of zirconium [12, 13], titanium [14], chromium [15], and nickel [16]. Moreover, based on iron complexes, some chiral reagents for organic synthesis [17], chiral analogs of DMAP [18, 19], chiral phosphines (Q-Phos, Walphos, *etc.*) [20, 21], and a class of chiral phosphites named ferrophites [22] were developed.

In the last two decades, the rhodium Cp complexes have been frequently used as catalysts for the C–H activation of aromatic compounds [23, 24]. However, the aryl-substituted derivatives are poorly studied. The rare examples include the synthesis of oxy-indoles *via* a three-component reaction between nitroarenes, alkynes, and carboxylic acid anhydrides [25], as well as the photo-induced C–H activation processes [26, 27]. Aryl-substituted cyclopentadienes have also been used in combination with RhCl₃ or [(cod)RhCl]₂ as a component of the catalytic system, in which the catalytically active species are generated *in situ* [28]. Recently we have demonstrated that rhodium complexes with simple and readily available phenyl-substituted Cp ligands, such as 1,2-C₅Ph₂H₃ and 1,2,4-C₅Ph₃H₂, can be significantly more efficient than *in situ* generated catalysts and even all previously known catalysts [29, 30].

Herein, using the example of the annulation of 4-methyl-*N*-(pivaloyloxy)benzamide with norbornene, we show that sometimes the reduced activity of phenyl-substituted cyclopentadienyl complexes of rhodium in C–H activation processes can be caused by their low solubility in organic solvents rather than the electronic or steric effects of the Cp ligand.

Results and discussion

The catalytic annulation of 4-methyl-*N*-(pivaloyloxy)benzamide with norbornene was carried out under the previously described conditions [31] and proceeded with absolute diastereoselectivity (Scheme 1). The reaction course was monitored by ^{1}H NMR spectroscopy. The structure of dihydroisoquinolone **1** was confirmed by NMR and X-Ray diffraction data (Fig. 1). We tested complexes [Cp^{Ph2}RhCl$_2$]$_2$ and [Cp^{Ph3}RhCl$_2$]$_2$ (Cp^{Ph2} = 1,2-C$_5$Ph$_2$H$_3$, Cp^{Ph3} = 1,2,4-C$_5$Ph$_3$H$_2$), as well as a classical catalyst [Cp*RhCl$_2$]$_2$ (Table 1). The first series of experiments using chloroform or methanol as solvents (entries 1, 3, and 5) showed notable superiority of [Cp*RhCl$_2$]$_2$ over the catalysts with Cp^{Ph3} and Cp^{Ph2} ligands in terms of activity. We initially assumed that one of the reasons for this behavior is the effect of the nature of the Cp ligand on the strength of the Rh–Cl bond, which must be broken by the action of CsOAc for the reaction to proceed. However, the DFT calculations using the EDA approach (see the Electronic supplementary information (ESI)) showed that the most active catalyst [Cp*RhCl$_2$]$_2$, on the contrary, has the strongest Rh–Cl bond among the complexes explored.

Another possible reason for the low activity of the Cp^{Ph3} and Cp^{Ph2} complexes may be their low solubility in organic solvents. Indeed, we showed that the addition of 10 mol % AgOAc to the reaction mixture results in immediate cleavage of the Rh–Cl bonds and the formation of soluble solvate complexes of rhodium, resulting in a significant increase in the catalytic activity (entries 2, 4, and 6). The simultaneous use of methanol as a solvent and AgOAc as an additive led to almost quantitative conversions for all the catalysts.

Conclusions

In summary, we showed that, when creating a catalytic system based on phenyl-substituted Cp ligands, the low solubility of complexes based on them should be taken into account, since it has a significant impact on the catalyst efficiency.

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Scheme 1. Reaction of 4-methyl-*N*-(pivaloyloxy)benzamide with norbornene.

Corresponding author

* E-mail: dloginov@ineos.ac.ru. Tel: +7(499)135-9308 (D. A. Loginov).

Electronic supplementary information

Electronic supplementary information (ESI) available online: the NMR spectra for the compound obtained and atomic coordinates for the optimized geometries. For ESI, see DOI: 10.32931/io2506a.
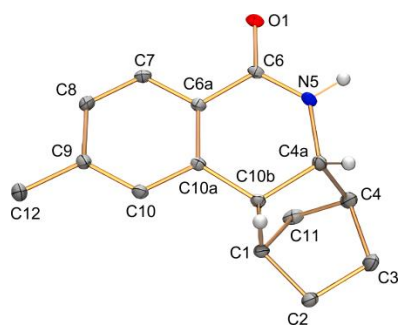

Figure 1. Molecular structure of **1** with atoms shown as thermal ellipsoids at 50% probability level. The hydrogen atoms (except three at C4a, C10b, and N5 atoms) are omitted for clarity.

Table 1. Catalyst screening for the annulation of 4-methyl-*N*-(pivaloyloxy)benzamide with norbornene

Entry	Cp^R	Additive	Conversion^a
1	Cp*	–	85 (99)
2	Cp*	AgOAc 10 mol %	92 (99)
3	Cp^{Ph3}	–	35 (50)
4	Cp^{Ph3}	AgOAc 10 mol %	86 (99)
5	Cp^{Ph2}	–	24 (26)
6	Cp^{Ph2}	AgOAc 10 mol %	80 (99)

^{a}the values in normal type are given for chloroform; the bracketed values are given for methanol.

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