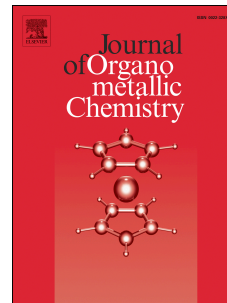


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Synthesis and reactivity of the cyclohexadienyl rhodium complexes

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Vavilova 28, Moscow, 119991, Russia. E-mail: dsp@ineos.ac.ru***Abstract**

In a search for an active catalyst for CH-activation reactions we have synthesized the half-sandwich rhodium complexes with a cyclohexadienyl ligand. In particular, the reaction of [(cyclooctene)₂RhCl]₂ with 1,3,5,5-tetramethylcyclohexadiene followed by addition of bromine gave the cyclohexadienyl polybromide complex [(η⁵-C₆H₃Me₄)RhBr₃]_n (**1**) in 73% yield. Treatment of **1** with ethylene converted it into the Rh(III) bromide complex [(η⁵-C₆H₃Me₄)RhBr₂]₂ (**2**), which is analogous to the classical catalyst [Cp*RhCl₂]₂. The reaction of **2** with 2 equiv. of 2-electron ligands L produced the expected adducts (η⁵-C₆H₃Me₄)RhBr₂L (L = ^tBuNC, pyridine, P(OMe)₃, PPh₃) in 80-90% yields. On the other hand, the reactions of **1** or **2** with excess of ^tBuNC led to complete replacement of the cyclohexadienyl ligand. The complex **2** was found to be inactive as catalyst (at 10 mol-% loading) for reactions of diphenylacetylene with benzoic acid, acetanilide, O-Boc-phenylhydroxamic acid, or benzophenone oxime. The absence of catalytic activity was attributed to the displacement of the cyclohexadienyl ligand.

Keywords: rhodium, cyclohexadienyl, half-sandwich complexes, CH-activation

1. Introduction

Rhodium(III) catalyzed CH-activation has attracted enormous attention in recent years [1]. While most of research has been done with the classical catalyst [Cp*RhCl₂]₂ (Scheme 1), other complexes with general formula [LRhX₂]₂ have also been investigated in attempt to reach higher activity and selectivity [2]. Recently, Rovis and Paton et al. have compared the catalytic activity of 22 rhodium complexes in the reaction of O-pivaloyl-phenylhydroxamic acid with 1-decene [3]. No simple correlation was found, although it appeared that electron-rich catalysts, such as [(1,3-diphenyl-tetrahydroindenyl)RhCl₂]₂, are the most active. On the other hand Tanaka et al. have shown that the electron-deficient catalyst [(C₅Me₃(COOEt)₂)RhCl₂]₂ is more active than the classical [Cp*RhCl₂]₂ in the reaction of acetyl anilines with alkynes [4]. This apparent contradiction may be resolved by speculation that electron-rich catalysts are more efficient for activation of electron-poor substrates and vice versa. However, a more general conclusion is that the activity of rhodium catalysts in CH-activation reactions is still difficult to predict. Bearing this in mind we decided to explore a new type of rhodium catalysts with a cyclohexadienyl ligand instead of the common cyclopentadienyl. Herein we report the results of this investigation.

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