



Note

Versatile and highly efficient synthesis of diruthenium tetrahydride complex

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ABSTRACT

A highly efficient and hydride reagent-free synthesis of diruthenium polyhydride cluster is reported. Salt metathesis followed by β -hydride elimination was the key reaction for introducing hydride. Heating Ru(III) complex, $[\text{Cp}^{\ddagger}\text{RuCl}_2]_2$ (**2a**, $\text{Cp}^{\ddagger} = 1,2,4\text{-tri-}t\text{-butylcyclopentadienyl}$), in 2-propanol in the presence of base afforded diruthenium tetrahydride complex, $\text{Cp}^{\ddagger}\text{Ru}(\mu\text{-H})_4\text{RuCp}^{\ddagger}$ (**1**), in nearly quantitative yield. Ruthenium halide complexes of different oxidation states were also converted to **1** under the same condition. These results suggest that the reaction mechanism proceeds via the reduction of ruthenium halide complexes, followed by salt metathesis and β -hydride elimination, and then hydrogen transfer from 2-propanol.

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1. Introduction

Transition metal polyhydride clusters have recently attracted considerable attention for their ability to activate inert bonds such as C–H and C–C in hydrocarbons [1], the C–O double bond of carbon dioxide [2], and the N–N triple bond of dinitrogen [3]. The metal–metal distances in polyhydride-bridged clusters are normally kept in the range of 2.4–2.9 Å. This enables the substrates to form multiple interactions with the metal centers when vacant sites are generated at the adjacent metal centers via dehydrogenation or hydride transfer. This multiple interaction between the substrates and the metal centers is probably the origin of the so-called “cluster effect,” namely concerted activation of the substrates due to the cooperative action of the metal centers. We are intensively studying the chemistry of multinuclear polyhydride clusters containing Cp^*Ru ($\text{Cp}^* = \text{pentamethylcyclopentadienyl}$) fragments, and have previously demonstrated its unique reactivity toward various substrates, including hydrocarbons [1,4], heterocyclic compounds [5], phosphines [6], and carbon dioxide [2,7]. Although the catalytic reactions of polyhydride clusters are still limited, their catalytic transformation utilizing their unique

reactivity would offer a new approach to chemical transformations.

One of the problems in constructing a catalytic cycle is the regeneration of the reactive hydride species, which is closely related to the synthesis of hydride complexes. Polyhydride clusters are usually synthesized by the reaction of transition metal halide complexes with main group hydrides such as LiAlH_4 , NaBH_4 , and LiHBEt_3 [1b,3b,8]. Although main group hydrides are useful tools for introducing hydrides, reactions with other substrates containing protic hydrogen often compete in reactions involving main group hydrides. Thus, metathetical reactions between transition metal halides and main group hydrides have limitations on functional group tolerance, which make regenerating hydride complexes under catalytic conditions difficult. Therefore, we extensively explored an alternative method for synthesizing polyhydride clusters without using main group hydrides. Since β -hydride elimination from an alkoxide ligand readily proceeds on a coordinatively unsaturated metal center, combination of salt metathesis with β -hydride elimination is a promising method to generate metal hydrides from metal halides under mild conditions. This method should also be effective for polyhydride clusters, particularly in the regeneration of hydrides in a catalytic cycle. We herein report a versatile and highly efficient synthesis of diruthenium tetrahydride complex in 2-propanol, proceeding via a key β -hydrogen elimination step.

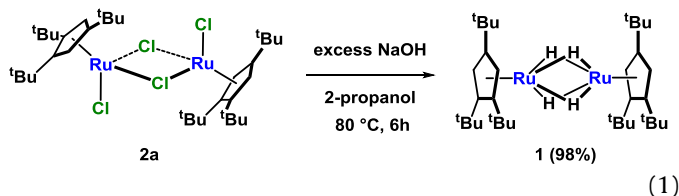
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2. Results and discussion

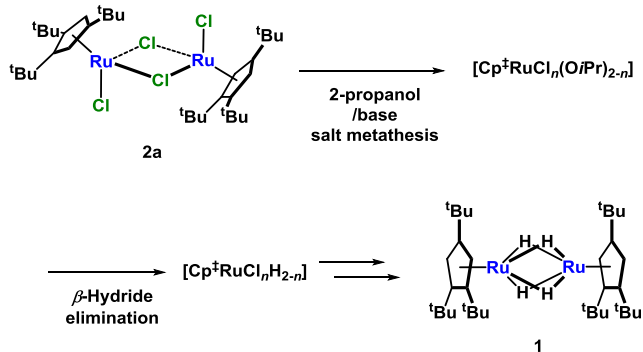
$\text{Cp}^{\ddagger}\text{Ru}(\mu\text{-H})_4\text{RuCp}^{\ddagger}$ (**1**) ($\text{Cp}^{\ddagger} = 1,2,4\text{-tri-}t\text{-butylcyclopentadienyl}$) [8g,9] was chosen as a probe due to its thermal stability, which prevents the side reaction (i.e. dimerization). This allows a thorough evaluation of the synthetic method. Chloride complexes containing $\text{Cp}^{\ddagger}\text{Ru}$ fragments with various oxidation states have been examined in detail. We focused on introducing alkoxide groups into the metal core, which would undergo β -hydride elimination leading to the formation of hydride (Scheme 1). We anticipated that a Ru(III) complex, $[\text{Cp}^{\ddagger}\text{RuCl}_2]_2$ (**2a**), would afford target compound **1** in 2-propanol in the presence of NaOH.

Complex **2a** and excess NaOH were dissolved in 2-propanol and the reaction mixture was stirred for 6 h at 80 °C. The brown suspension first turned to a red-purple solution, and finally to a red solution. After the solution was filtered to remove NaCl and the remaining NaOH, the filtrate was purified by column chromatography on alumina. The desired product, $\text{Cp}^{\ddagger}\text{Ru}(\mu\text{-H})_4\text{RuCp}^{\ddagger}$ (**1**), was obtained in 98% yield. The reaction proceeded more effectively than with main group hydrides such as LiAlH_4 and LiHBET_3 [9].



Previously, **1** was synthesized by reacting halide complexes with excess LiAlH_4 , NaBH_4 , or LiHBET_3 . The reaction with main group hydrides most certainly proceeds *via* the formation of intermediates, aluminato- or borohydride adduct, and subsequent protonolysis, to form **1** [10]. The conversion and selectivity of the protonolysis are highly dependent on the main group hydrides used. In addition, aluminum and boron compounds formed by the protonolysis of a main group hydride induce the side-reaction and decrease the yields of **1**. In contrast, the improved method using 2-propanol in the presence of base produces only acetone as a by-product, which is inert toward **1**. As a result, this method enables a more efficient access to **1**.

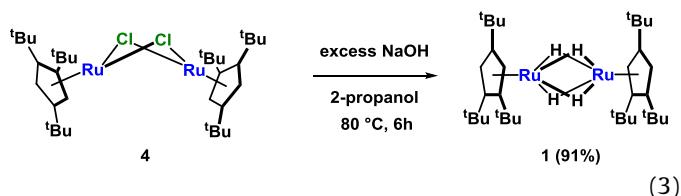
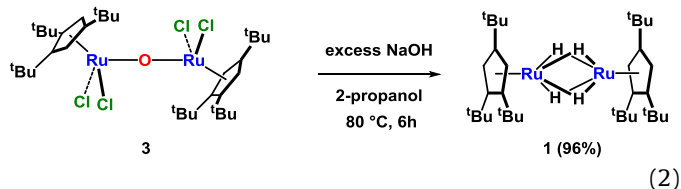
The most probable route to **1** is shown in Scheme 1. The four hydrides in **1** are introduced consecutively *via* salt metathesis of 2-propoxide, followed by β -hydride elimination. The Ru(III) complex (**2a**) undergoes several types of redox reactions under neutral or acidic conditions in alcoholic solvents [9]. For example, air oxidation of **2a** affords a Ru(IV) complex, $[\text{Cp}^{\ddagger}\text{RuCl}_2(\mu\text{-O})]_2$ (**3**), while thermolysis of **2a** in 2-propanol affords a Ru(II) complex, $[\text{Cp}^{\ddagger}\text{RuCl}]_2$ (**4**). This reactivity inspired us to develop a new route involving



Scheme 1. Working hypothesis of 2-propanol/base synthesis of **1**.

redox steps. Thus, we examined the reaction of Ru(IV) and Ru(II) complexes, **3** and **4**, respectively, with 2-propanol in the presence of bases.

Complex **3** and excess NaOH were dissolved in 2-propanol and the mixture was stirred for 6 h at 80 °C. The red suspension first turned to a red-purple solution, and finally to a red solution. Complex **1** was obtained from the resulting mixtures in 96% yield (Eq. (2)) [11]. Similarly, complex **4** was converted into **1** in 91% yield (Eq. (3))



In both cases, complex **1** was obtained in excellent yield. These results can be rationalized by the ability of ruthenium complexes to readily change the oxidation state. Koelle and co-workers reported, in detail, the reduction of ruthenium complexes in an alcoholic solvent in the presence of a base [12]. The Ru(III) complex $[\text{Cp}^*\text{RuCl}_2]_2$ (**2b**) is readily reduced to the Ru(II) complex $[\text{Cp}^*\text{Ru}(\text{OMe})]_2$ (**5a**) in methanol in the presence of K_2CO_3 at ambient temperature. Complex **5a** underwent β -hydride elimination under thermal conditions to afford $\text{Cp}^*\text{Ru}(\mu\text{-CO})(\mu\text{-H})_2\text{RuCp}^*$ (**6**) [13]. The above mentioned redox processes of the Ru complexes having a Cp^* auxiliary show that Cp^{\ddagger} analogue **2a** most certainly reacts with 2-propanol in the presence of a base to generate $[\text{Cp}^{\ddagger}\text{Ru}(\text{Oi-Pr})]_2$ as an intermediate. The fact that **1** was obtained from complex **4** supports the following redox path.

The reaction mechanism for the formation of **1**, starting from a series of chloride complexes, is summarized in Scheme 2. We previously reported that both **3** and **2a** afforded complex **4** upon heating in 2-propanol under neutral conditions [9]. This strongly implies that the reaction in the 2-propanol/base method involves the reduction of **3** and **2** to **4** in the initial stage of the reaction. The two chloride ligands in **4** are then displaced by 2-propoxide ligands to generate an intermediate, $[\text{Cp}^{\ddagger}\text{Ru}(\text{OiPr})]_2$ (**A**). Koelle and Severin independently reported the formation of analogous dinuclear ruthenium methoxo complexes, $[\text{CpsRu}(\text{OMe})]_2$ (**5**; $\text{Cps} = \text{Cp}^*$ or 1-methoxy-2,4-di-*t*-butyl-3-neopentylcyclopentadienyl), from Ru(III) complexes in methanol in the presence of a base [12,14]. Tilley also reported the synthesis of **5** from a Ru(II) complex, $[\text{Cp}^*\text{RuCl}]_4$ (**7**), under the same conditions [15]. This precedent strongly suggests the formation of **A**, and it is plausible that β -hydride elimination from the 2-propoxide ligands in **A** provides dihydride intermediate **B**. In the final stage of the reaction, we propose that two hydrogen atoms transfer from 2-propanol to dinuclear species **B**. The details of this process are still unclear, but oxidative addition of O–H of 2-propanol to the highly unsaturated 28e-Ru center of **B**, followed by β -hydride elimination, seems highly plausible. Methine C–H addition of 2-propanol could be an alternative pathway, but less likely owing to the steric demands of Cp^{\ddagger} ligands. In contrast, oxidative addition of the O–H bond occurs readily *via* a heterolytic pathway, involving the nucleophilic attack

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