



Reaction of a polyphosphino ruthenium(II) acetate complex with Grignard reagents: Halogenation, alkylation and β -elimination

Joseph J. Gair^a, Alexi J. Young^a, Jeremiah J. Scepaniak^a, Peter M. Simone^a, Chen T. Chau^a, Alicia A. Peterson^a, Elizabeth M. Nessel Ferguson^a, Williamson N. Oloo^a, Daniel T. Welna^a, Jonathan I. Siverson^a, Lothar M. Stahl^b, Chris P. Schaller^{a,*}

^a Department of Chemistry, College of Saint Benedict/Saint John's University, St. Joseph, MN 56374, USA

^b Chemistry Department, University of North Dakota, Grand Forks, ND 58202-9024, USA

ARTICLE INFO

Article history:

Received 7 August 2015

Received in revised form

16 October 2015

Accepted 19 October 2015

Available online 22 October 2015

Keywords:

Phosphine complexes

Hydride complexes

Ruthenium(II)

Grignard reagents

ABSTRACT

(PMe₃)₄Ru(H)OAc has been prepared from (PPh₃)₃Ru(H)OAc via phosphine exchange followed by solvent partitioning between acetonitrile and pentane. Complexes of the type (PMe₃)₄Ru(H)R (R = Et, ⁿPr, ⁿBu, ⁱBu, H) have been synthesized through reaction with the corresponding Grignard reagents, RMgCl, and were found to be moderately stable provided the alkyl group is primary. Treatment with bulkier alkyl-magnesium chlorides led instead to the dihydrido complex (PMe₃)₄RuH₂. In some cases, the reaction was complicated by transfer of halide from the Grignard reagent to form, for example, (PMe₃)₄Ru(H)Cl.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Transition metal alkyl hydride complexes are critical intermediates in the activation of C–H bonds through oxidative addition [1]. These intermediates are also invoked in mechanistic schemes for a number of other processes, such as alkene hydrogenation and hydroformylation [2]. Frequently, indirect evidence strongly suggests the presence of alkyl hydrides along a reaction pathway, most notably from studies showing H/D exchange in hydrocarbons in the presence of transition metal complexes [3]. These intermediates are infrequently observed because of their relative instability toward reductive elimination, beta-elimination and other reactions. The synthesis of alkyl hydride complexes is crucial to gain insight into the behavior of these elusive intermediates.

A number of methods have been applied to the synthesis of alkyl hydride complexes (Scheme 1). Direct synthesis via the oxidative addition of hydrocarbons may be the most germane approach given the principal focus on C–H activation intermediates. This technique has been applied in a number of cases in which the resulting alkyl

hydrides are particularly stable [4]. In some cases, polydentate ancillary ligands such as tris(pyrazolyl)borates or PNP-type pincer ligands stabilize these compounds by preventing ligand dissociation [5], as coordinative unsaturation is often required prior to reductive elimination [6]. However, stable 16-electron complexes of this type have also been made in this way, as have relatively labile polyphosphino complexes [4c,6b].

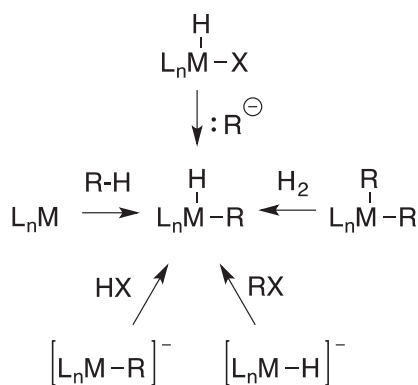
Alkyl hydrides have also been prepared in less direct ways that do not involve oxidative addition. Protonation of metal alkyls is probably the most commonly used of these alternative techniques [7]. This approach has been employed with square planar platinum(II) and iridium(I) alkyls; usually, the additional coordination by a counterion or by solvent results in an octahedral species [8]. Octahedral alkyl hydride complexes have also been obtained via protonation of anionic five-coordinate alkyls [9]. In contrast, use of a non-coordinating counterion during protonation of a square planar iridium compound has allowed the isolation of a five-coordinate cationic species [6a].

Other methods include hydrogenolysis of metal alkyls, accompanied by loss of alkane [10], the alkylation of hydride complexes containing labile anionic ligands [6b,9], and the treatment of anionic metal hydride complexes with alkyl triflates [6c].

Significant attention has been paid to the study of the alkyl hydrides of d [6] iridium(III) and platinum(IV), owing to the

* Corresponding author.

E-mail address: cschaller@csbsju.edu (C.P. Schaller).



Scheme 1. Approaches to alkyl hydride complexes.

importance of d [8] iridium(I) and platinum(II) complexes in carbon-hydrogen bond-cleaving events leading to alkane dehydrogenation and oxygenation, respectively [3a]. There have also been studies of d [6] complexes of osmium(II) and ruthenium(II) [4c,11]. The latter cases deserve additional consideration because of the prominent role of ruthenium catalysts in synthetic organic reactions [12].

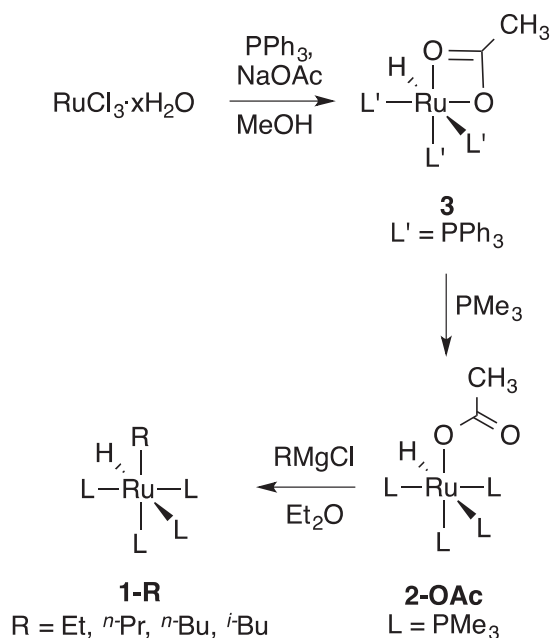
We have undertaken synthetic studies leading to a series of different ruthenium alkyl hydrides, $(\text{PMe}_3)_4\text{Ru}(\text{H})\text{R}$ (**1-R**). Several compounds of this type have been synthesized previously, from the corresponding alkyl halides [13], hydrido halides [14], dihalides [15], or, in the case of **1-Ph**, from the corresponding benzyne complex [11]. Although some of these compounds have been reported previously, they have been prepared by disparate methods that do not lend themselves easily to the synthesis of new derivatives. A simplified synthetic scheme reported herein allow a variety of compounds to be prepared from a common synthetic intermediate. The result is an approach that provides selected ruthenium alkyl hydrides in three steps from commercially available materials.

2. Results and discussion

The goal of this work was to develop an easily accessible synthon that could be derivatized in one step to afford a variety of ruthenium alkyl hydrides. The polyphosphino compounds $(\text{PMe}_3)_4\text{Ru}(\text{H})\text{R}$ (**1-R**) were selected as synthetic targets. Some members of this family of compounds have previously been demonstrated to undergo reductive elimination to give alkanes at moderately elevated temperatures, and so it seemed reasonable that additional derivatives would also be relatively stable [11].

Owing to the reported difficulty of working with the highly insoluble $(\text{PMe}_3)_4\text{Ru}(\text{H})\text{Cl}$ [11], a similar synthon possessing an alternative labile, anionic ligand for displacement by alkylating agents was sought. One possibility was to use an acetate as a leaving group (Scheme 2). The triphenylphosphine complex, $(\text{PPh}_3)_3\text{Ru}(\text{H})\text{OAc}$ (**3**), was easily prepared from commercially available materials [16], and replacement of the triphenylphosphine ligands with the more strongly donating trimethylphosphine was expected to afford **2-OAc**.

Heating an orange slurry of **3** in toluene in the presence of excess trimethylphosphine quickly resulted in dissolution of solid and bleaching of the solution to a pale yellow color. Separation of **2-OAc** from liberated triphenylphosphine at first proved challenging. Sublimation was fruitless, and attempts at recrystallization were stymied by co-crystallization of PPh_3 with **2-OAc**. A number of chromatographic approaches also failed; **2-OAc** either failed to elute or else decomposed on the column. Solvent partitioning

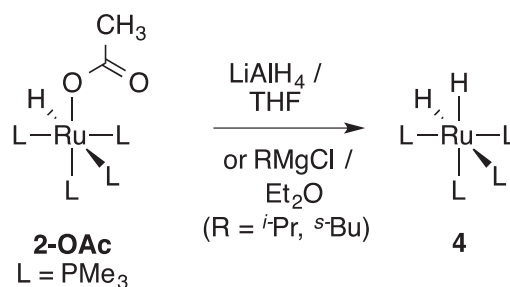


Scheme 2. A new approach to compounds **1-R**.

between acetonitrile and pentane produced more satisfactory results. Evaporation of the acetonitrile fraction produced almost quantitative yield of a waxy solid. ^1H NMR analysis revealed a downfield shift of the hydride resonance from -18 ppm observed in **3** to -8.5 ppm (See Appendix A). The complex splitting pattern of this hydride peak, an apparent doublet of quartets, and the 2:1:1 triplet:doublet:doublet A_2BC pattern in the methyl region were consistent with *cis*-octahedral geometry [13]. Further purification through recrystallization proved unreliable as trace amounts of triphenylphosphine remained in the samples.

The minor impurity in this material did not prevent its successful reaction with nucleophiles. Treatment of **2-OAc** with LiAlH_4 in THF led to formation of the dihydrido complex $(\text{PMe}_3)_4\text{RuH}_2$ (**4**, Scheme 3). Inspection of ^1H NMR data showed a triplet and doublet consistent with bound trimethylphosphine with an integration ratio 18:18 as well as an apparent doublet of triplets at -9.73 ppm integrating to 2H [17].

The fact that saturated alkyl complexes (methyl, ethyl and propyl) had already been reported in this system suggested that targeting similar compounds would be a suitable next step for developing a general synthetic method. Longer-chain alkyl ligands on transition metals are relatively rare because of their potential to undergo β -elimination. They have been reported in complexes with supporting tris(pyrazolyl)borate ligands, in which case the chelation effect probably hinders ligand dissociation required to open a



Scheme 3. New synthesis of $(\text{PMe}_3)_4\text{RuH}_2$.

Download English Version:

<https://daneshyari.com/en/article/1323065>

Download Persian Version:

<https://daneshyari.com/article/1323065>

[Daneshyari.com](https://daneshyari.com)