Inorganica Chimica Acta 375 (2011) 128–134

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Oxidative addition of methyl iodide to [Rh($CH_3COCHCOCH_3$)(CO)(P($(OCH_2)_3CCH_3$))]

J.J.C. Erasmus, Jeanet Conradie *

Department of Chemistry, University of the Free State, Bloemfontein 9301, South Africa

ARTICLE INFO

Article history:
Received 13 January 2010
Received in revised form 28 March 2011
Accepted 26 April 2011
Available online 1 May 2011

Keywords:
Acetylacetone
Rhodium
Oxidative addition
Phosphite
DFT

ABSTRACT

The reaction rate of the oxidative addition and the following CO insertion step of methyl iodide with [Rh(acac)(CO)(P($(OCH_2)_3CCH_3$))] is determined. The key finding is that while [Rh(acac)(CO)(P($(OCH_2)_3CCH_3$))] oxidatively adds methyl iodide *ca* 300 times faster than the Monsanto catalyst, the CO insertion step is much slower. However, the rate-determining step of the oxidative addition reaction of the phosphorus-containing acetylacetonato-rhodium(I) complex, the carbonyl insertion step, is still in the same order or faster than the rate-determining oxidative addition step of iodomethane to $[Rh(CO)_2I_2]^-$.

1. Introduction

Oxidative addition of organic molecules to unsaturated transition metal complexes is a fundamental process in organometallic chemistry and plays a key role in many important catalytic reactions [1]. An important example is the reaction between methyl iodide and *cis*-$[Rh(CO)_2I_2]^-$, the rate-determining step in the rhodium based Monsanto carbonylation of methanol to acetic acid [2–4]. However, the rate-determining step in the iridium based Cativa industrial process for the production of acetic acid is the CO insertion [5]. It has previously been shown that some β-diketonato complexes of rhodium(I) can facilitate the formation of acyl species during oxidative addition of methyl iodide to complexes of the type [Rh(β-diketonato)(CO)(PPh_3)] [6,7]. As these complexes invariably contained at least one carbonyl ligand, it was found that most of the oxidative addition reactions were complicated by alkyl–acyl conversion reactions [8–11]. Characterization of the final products (alkyl versus acyl) and an understanding of the factors influencing these conversion reactions, are thus of primary importance. Van Zyl et al. [12] reported the first study concerned with the oxidative addition of iodomethane to bisphosphite complexes of the type [Rh(β-diketonato)($P(OPh)_3)_2$]. The absence of a carbonyl ligand in these complexes led to an expected less complex mechanism in terms of the absence of the carbonyl insertion step [13]. The current study describes the synthesis and oxidative addition of iodomethane to the monophosphite complex [Rh(acetylacetonato)(CO)(P($(OCH_2)_3CCH_3$))], this being novel in terms of Rh(I) substrates containing a *single* phosphite ligand (phosphites tend to replace both carbonyl groups giving a bis(phosphite) as final product).

2. Results and discussion

2.1. Synthesis and identification of complexes

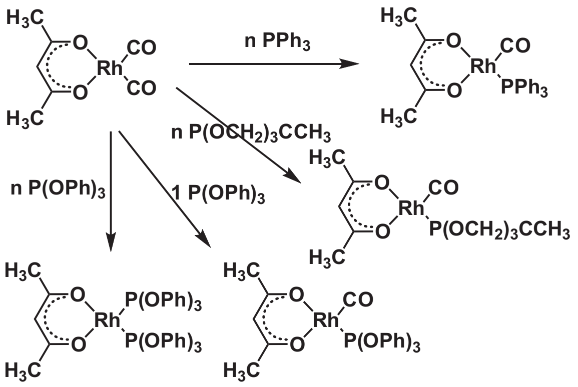
Only one CO group is exchanged for PPh_3 in [Rh(acac)$(CO)_2$], even with the addition of an excess PPh_3 [15] (acac = acetylacetonato). However, the main product of the corresponding reaction with triphenylphosphite $P(OPh)_3$ is [Rh(acac)$(P(OPh)_3)_2$]. With less than 2 mol of $P(OPh)_3$, [Rh(acac)(CO)($P(OPh)_3$)] was produced [16]. Strong π-acceptors such as $PR_3 = P(OPh)_3$ are necessary in order to obtain di-substituted [Rh(acac)$(PR_3)_2$]. Weak π-acceptors, such as PPh_3, even when used in large excess, afford only monosubstituted products [17]. The phosphite 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane ligand with a Tolman electronic parameter[1] of $\nu(CO) = 2087.3\ cm^{-1}$ similar to that of $P(OPh)_3$ ($2085.3\ cm^{-1}$) is expected to exhibit a strong π-accepting ability [18]. The new bright yellow [Rh(acac)(CO)(P($(OCH_2)_3CCH_3$))] complex with only one CO group displaced, was obtained in a high yield by slowly adding *ca* 1.2 equivalents of $P(OCH_2)_3CCH_3$ to [Rh(acac)$(CO)_2$].

---

* Corresponding author. Tel.: +27 51 401 2194; fax: +27 51 444 6384.
E-mail address: conradj@ufs.ac.za (J. Conradie).

[1] The Tolman electronic parameter of PR_3 is the frequency of $Ni(CO)_3(PX1X2X3)$, with X1X2X3 = Ph_3, OPh_3, $(OCH_2)_3CCH_3$, etc.

0020-1693/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2011.04.041



The electronic structure and reactivity of Rh(I) complexes, which show catalytic activity, can be modified by the selection of the appropriate σ or π donor–acceptor ligands. PPh_3 is a strong σ donating but weak π acceptor ligand, whereas $P(OPh)_3$ is a strong π acceptor [15]. The π acceptor ability of $P(OCH_2)_3CCH_3$ is demonstrated in comparing the carbonyl stretching frequency of $[Rh(acac)(CO)(P(OCH_2)_3CCH_3)]$ (ν(CO) = 1998 cm^{-1} (KBr), 2008 cm^{-1} (CH_3Cl solution)) with that observed in the case of the triphenylphosphine analog (ν(CO) = 1975 cm^{-1}). Back donation to the phosphite ligand tends to reduce electron density on the central metal atom to a larger extent compared to PPh_3 leading to a weakened ability to reduce the CO bond order in the case of the title compound. The strong delocalization of electron density away from the metal center in the phosphite complex is expected to have a marked influence on the reactivity of the rhodium metal towards, for example, oxidative addition, where the metal acts as a Lewis base. A progressively slower oxidative addition rate is thus expected when going from $[Rh(acac)(CO)(PPh_3)]$ (ν(CO) = 1975 cm^{-1}) to $[Rh(acac)(CO)(P(OCH_2)_3CCH_3)]$ (ν(CO) = 1998 cm^{-1}) to $[Rh(acac)(CO)(P(OPh)_3)]$ (ν(CO) = 2006 cm^{-1}) [15].

2.2. Kinetics

2.2.1. Infrared study

Kinetic measurements for the reaction progress between CH_3I and $[Rh(acac)(CO)(P(OCH_2)_3CCH_3)]$ in $CHCl_3$ were first carried out using IR spectroscopy by monitoring the changes in absorbance of peaks at different ν(CO) bands in the range of 1650–2200 cm^{-1}. This technique is ideal to distinguish between CO bonds in metal-CO complexes of Rh^I-carbonyl complexes, Rh^{III}-carbonyl complexes and CO bonds in metal-$COCH_3$ complexes of Rh^{III}-acyl complexes [19]. A typical series of the spectra of the oxidative addition reaction of CH_3I to $[Rh(acac)(CO)(P(OCH_2)_3CCH_3)]$ as well as the subsequent carbonyl insertion step, are shown in Fig. 1. The *first* reaction step shows that the disappearance of the Rh^I-CO complex (at 2008 cm^{-1}, $k_{obs} = 4.75(8) \times 10^{-3}\ s^{-1}$) basically corresponds to the formation of the Rh^{III}-CO complex (at 2104 cm^{-1}, $k_{obs} = 5.31(8) \times 10^{-3}\ s^{-1}$). The band at 2104 cm^{-1} is assigned to a Rh^{III}-alkyl product $[Rh(acac)(CO)(P(OCH_2)_3CCH_3)(CH_3)(I)]$. The half-life of this reaction is 138 s and this reaction goes to completion, *i.e.* all Rh(I) is converted to the first Rh^{III}-alkyl product.

A *second* much slower ($t_{1/2} \approx 15$ h) reaction, as observed on the IR, also illustrated in Fig. 1, shows that the formation of the Rh^{III}-$COCH_3$ species (at 1714 cm^{-1}, $k_{obs} = 12.6(8) \times 10^{-6}\ s^{-1}$) and corresponds to the depletion of the Rh^{III}-CO signal (at 2104 cm^{-1}, $k_{obs} = 12.8(8) \times 10^{-6}\ s^{-1}$). The Rh^{III}-acyl results from the migratory insertion of the methyl group of the Rh^{III}-alkyl to the carbonyl group. By comparing the rate constants, the *second reaction* is $0.005/0.000013 \approx 385$ times slower than the *first reaction* for $[CH_3I] = 0.30\ mol\ dm^{-3}$. Since the *second reaction* is much slower than the *first reaction*, it was treated in isolation. Data from the interface at the boundary between the two reactions were, however, disregarded. This *second reaction* was found to be independent of $[CH_3I]$. The kinetic data of the *first* and *second* reaction steps are consistent with

$$Rh^{I} + CH_3I \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Rh^{III}\text{-alkyl} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Rh^{III}\text{-acyl}$$

with $k_{-1} \approx 0 \approx k_{-2}$.

2.2.2. UV–Vis, solvent and temperature dependence study

The reaction between CH_3I and $[Rh(acac)(CO)(P(OCH_2)_3CCH_3)]$ in $CHCl_3$ was also monitored on an UV–Vis spectrophotometer and both reaction steps could be identified. The reaction rate constant obtained for the first step corresponded to the rate constant for the disappearance of the Rh^I monocarbonyl species as observed by IR. The rate constant for the second step corresponded to the rate constant for the formation of the Rh^{III}-acyl species, the *second reaction* as observed on the IR spectrophotometer.

Plots of k_{obs} versus $[CH_3I]$ for the *first reaction* in chloroform are linear (Fig. 2), indicating the reaction to be first order in CH_3I and hence second order overall. This result is consistent with the rate expression:

$$k_{obs} = k_1[CH_3I] + k_{-1}, k_{-1} \rightarrow 0$$

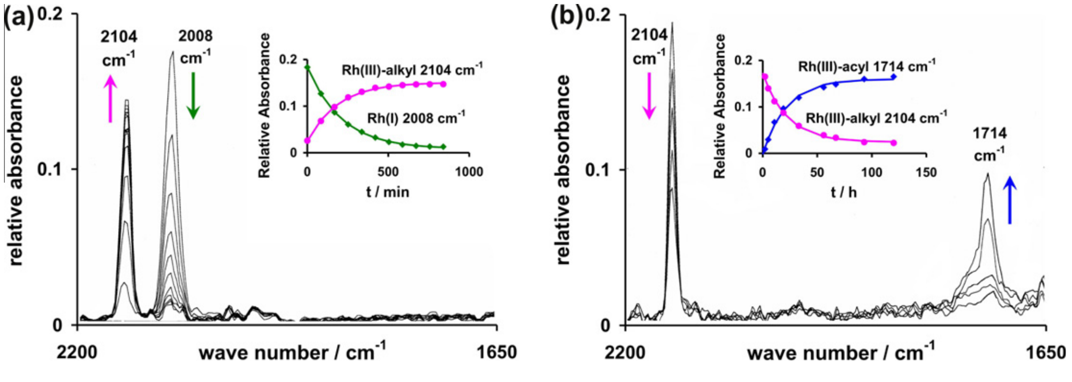


Fig. 1. Illustration of the oxidative addition reaction between CH_3I and $[Rh(acac)(CO)(P(OCH_2)_3CCH_3)]$ as monitored on the IR spectrophotometer between 1650 and 2200 cm^{-1} in chloroform at 25 °C. (a) The *first reaction* (left, 84 s intervals) is indicated by the disappearance of Rh^I (peak at 2008 cm^{-1}) and the simultaneous appearance of Rh^{III}-alkyl (peak at 2104 cm^{-1}) at the same rate. (b) The *second reaction* (selected scans at t = 0, 2, 5, 10.75 and 19 h are shown) is indicated by the simultaneous disappearance of Rh^{III}-alkyl (peak at 2104 cm^{-1}) and the formation of an Rh^{III}-acyl (peak at 1714 cm^{-1}) species. The inserts give the absorbance vs. time data of the indicated species. $[CH_3I] = 0.2963\ mol\ dm^{-3}$, $[Rh] = 4 \times 10^{-3}\ mol\ dm^{-3}$.