Inorganic Chemistry Communications 21 (2012) 43–46

Contents lists available at SciVerse ScienceDirect

Inorganic Chemistry Communications

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

A Mechanistic Description of Unexpected Room Temperature C-H and P-C Bond Activation by Wilkinson's Catalyst

Elvin Igartúa-Nieves, Antonio J. Rivera-Brown, José E. Cortés-Figueroa *

Organometallic Chemistry Research Laboratory, Department of Chemistry, University of Puerto Rico, Mayagüez, PR 00681-9019

ARTICLE INFO

Article history:
Received 25 January 2012
Accepted 15 April 2012
Available online 24 April 2012

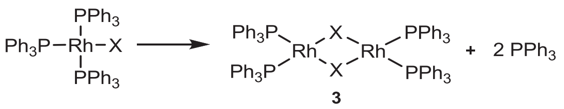
Keywords:
Wilkinson's catalyst
Consecutive reactions
C-H bond activation
oxidative addition
reductive elimination
metal hydride

ABSTRACT

The Wilkinson's catalyst, (PPh3)3RhCl dissolved in benzene under nitrogen or under high vacuum undergoes a series of unreported reactions at room temperature. The preliminary mechanistic description involves a series of consecutive intramolecular and intermolecular phosphine exchanges, benzene oxidative addition, and biphenyl reductive elimination.

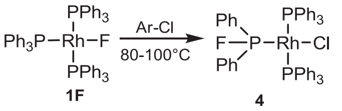
Introduction

The Wilkinson's catalyst, $(PPh_3)_3RhCl$ (**1Cl**), is ubiquitous in inorganic synthesis and in homogeneous catalysis [1]. However, key mechanistic information concerning structure-reactivity relationship of its reactions in aromatic solvents remains unravel. The fluoro analogue of **1Cl**, $(Ph_3P)_3Rh(X)$ (**1 F,** X = F) [2], was recently prepared and characterized along with the assessment of its reactivity promoted by reversible intramolecular Rh-F/P-Ph exchange [3] producing *cis*-$(Ph_3P)_2Rh(Ph)(Ph_2PX)$ (**2 F**, X = F). The chemical species **1Cl** and its fluoro analogue **1 F** are somewhat similar in terms of their structure and reactivity [2,3]. For example, they exhibit similar geometry parameters in the solid state, and formation of the bridged dimers $(Ph_3P)_4Rh_2(\mu\text{-}X)_2$ (X = F, Cl) (**3**) upon PPh_3 dissociation (Eq. (1)).



(1)

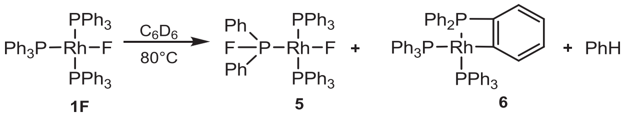
It was reported that unlike **1Cl** that was thought to produce $(Ph_3P_2)_4Rh_2(\mu\text{-}Cl)_2$ (**3Cl**) and traces of $(Ph_3P)_2(Ph)Rh(Cl)_2$ as the sole products when dissolved and heated in aromatic solvents, **1 F** exhibits a series of unexpected reactions [2]. Reactions of **1 F** with Ar-Cl (Ar = Ph, p-tolyl) produce *trans*-$(Ph_3P)_2Rh(Ph_2PF)(Cl)$ (**4**) and Ar-Ph (Eq. (2)).



(2)

In C_6D_6 **1 F** produces *trans*-$(Ph_3P)_2Rh(Ph_2PF)(F)$ (**5**) and $(Ph_3P)_2Rh(\eta^2\text{-}(C_6H_4PPh_2))$ (**6**) (Eq. (3)) [2].

It was proposed that reactions 3 and 4 proceed via rate determining reversible intramolecular P-Ph/Rh-F exchange (Eq. (2)) [2,3].



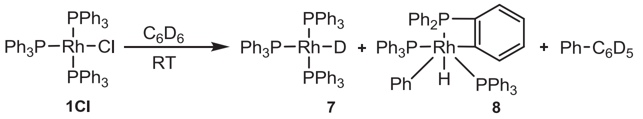
(3)

In the present communication we are reporting that **1Cl** exhibits a similar activity under milder conditions than reported for **1 F**. In addition to formation of the chloro-bridged dimer (**3Cl**), **1Cl** undergoes a series of reactions when it is dissolved in benzene (or in C_6D_6) at room temperature under nitrogen or under high vacuum. However, unlike **1 F** that produces *trans*-$(Ph_3P)_2Rh(Ph_2PF)(F)$ (**5**) and $(Ph_3P)_2Rh(\eta^2\text{-}(C_6H_4PPh_2))$ (**6**) when it is dissolved in C_6D_6, **1Cl** produces $(Ph_3P)_3Rh(D)$ (**7**), $(Ph_3P)_2Rh(\eta^2\text{-}(C_6H_4PPh_2))(Ph)(H)$ (**8**) and Ph-C_6D_5 when it is dissolved in C_6D_6 (Eq. (4)).

---

* Corresponding author.
E-mail address: jose.cortes.figueroa@usa.net (J.E. Cortés-Figueroa).

1387-7003/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2012.04.006



(4)

Experimental

The nature of the chemical species was established by ^{1}H NMR spectroscopy. The reactions' progresses were monitored by observing the decrease of absorbance values at 370 nm. Plots of absorbance vs. time were biexponential consisting of two consecutive absorbance decays: a relatively rapid absorbance decay (referred as the fast segment of the plot) followed by a relatively slow absorbance decay (referred as the slow segment of the plot) (Fig. 1).

Consecutive pseudo-first order rate constant values were determined in triplicate by fitting the absorbance vs. time plots using a non-linear curve program (*OriginPlus 7.5™*). Error limits of the average rate constant values and of the activation parameters, reported in Table 1 of *supporting information* are given in parentheses as the uncertainties of the last digit(s). Following the reactions' progresses by ^{1}H NMR spectroscopy permitted correlation of the segments of the biexponential plots to specific chemical processes.

Results and Discussion

The biexponential plots of absorbance vs. time of solutions of **1Cl** in benzene are shown in Fig. 1. The nature of the chemical processes involved in the fast and slow segments of the plots depends on the experimental conditions (*vide infra*). For example, for reactions of **1Cl** with benzene, the fast and slow segments of the plots were correlated to consecutive reconversion of **1Cl** from **3Cl** and intramolecular P-Ph/Rh-Cl exchange [2] on **1Cl** producing **2Cl**, respectively (Eq. (5)). It is being proposed that the hydrido and Ph_2 species are respectively produced by a parallel intramolecular oxidative addition (cyclometalation) and intermolecular oxidative addition of benzene to $(Ph_3P)_3Rh(Ph)$ (**9**), that in turn is produced by intermolecular PPh_3/PPh_2Cl exchange on **2Cl** (Eq. (6)). The basis for this interpretation rests on aspects of the reported mechanism for the reactions of **1 F** with Ar-X (X = H, Cl) [2] and on results from kinetics experiments being reported in this communication.

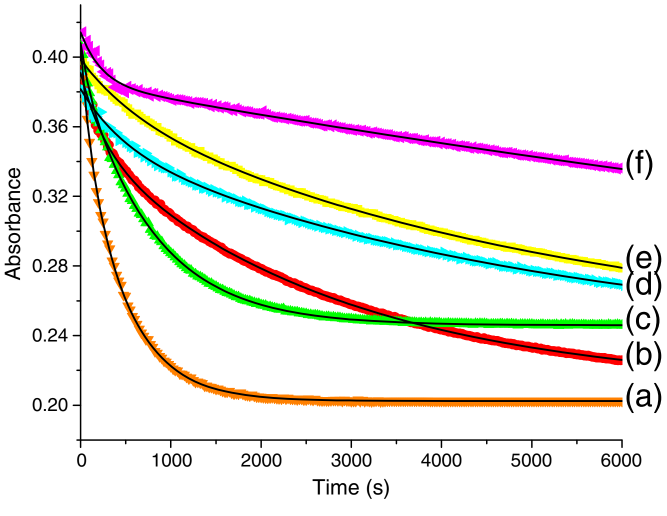
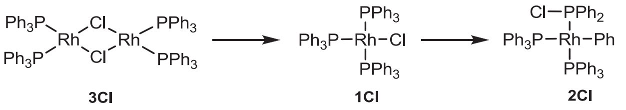
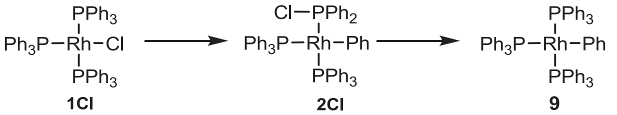


Fig. 1. Plots of absorbance (370 nm) vs. time for reactions of **1Cl** with benzene. (a), at 62.1 °C; (b), at 42.1 °C; (c), at 56.1 °C; (d), at 32.1 °C in presence added $[PPh_3]_{added} = 2.29 \times 10^{-4}$ M; (e), at 32.1 °C; (f), at 32.1 °C in presence added $[PPh_3]_{added} = 7.37 \times 10^{-3}$ M.



(5)



(6)

The set of consecutive reactions in Eqs. (5) and (6) can be expressed as a general set of consecutive first order reactions (Eq. (7)) where R is the reactant, I is a non-steady state intermediate, P is the product(s), and k_{obsd} and k'_{obsd} are pseudo-first-order rate constants [4]. Eq. (8) is the corresponding integrated and evaluated form of the rate law when absorbance is used to monitor the reaction's progress. In Eq. (8), A_t and A_∞ are absorbance at time t and at time infinity, respectively, and the coefficients α and β are constants whose values depend on k_{obsd}, k'_{obsd}, and on the extinction coefficients of the chemical species involved in the consecutive reactions [4].

$$R \xrightarrow{k_{obsd}} I \xrightarrow{k'_{obsd}} P \tag{7}$$

$$A_t = \alpha e^{-k^t_{obsd}} + \beta e^{-k'^{t}_{obsd}} + A_\infty \tag{8}$$

The observed biexponential decay of absorbance with time is mathematically described by Eq. (8). A detailed explanation about why correlation of k_{obsd} and k'_{obsd} to specific chemical reactions depends on experimental conditions and how the actual assignment was achieved will be deferred until the next two paragraphs. Results from experiments where the reactions of **1Cl** with C_6D_6 were monitored by ^{1}H NMR spectrometry evidenced formation of uncoordinated PPh_3 (Fig. 2). Observation of free PPh_3 is consistent with formation of **3Cl.** Interestingly, formation of C_6D_5-Ph and a Rh-H hydride was observed only under flooding conditions where $[PPh_3]_{added} >> [\mathbf{1Cl}]_0$ ($[\mathbf{1Cl}]_0$ = initial **1Cl** concentration). The interpretation of these observables is that oxidative addition of C_6D_6 to **2Cl** followed by reductive elimination accounts for the formation of C_6D_5-Ph. In turn, the hydrido species is formed from **9**. The basis for this interpretation rests on the observation that ^{1}H NMR spectra of solutions containing **1Cl** and added PPh_3 in C_6D_6 displays signals corresponding to C_6D_5-Ph and a Rh-H hydride. The absence of these ^{1}H NMR signals obtained four hours after **1Cl** was dissolved in C_6D_6 without added PPh_3 suggests that C_6D_5-Ph and the hydrido species are formed exclusively from **9** during the time scale of this study. Oxidative addition of C_6D_6 to **9** followed by reductive elimination forming $(Ph_3P)_3Rh(D)$ (**7**) accounts for formation of C_6D_5-Ph but not for the formation of Rh-H hydride (Eq. (6)). However, intramolecular oxidative addition on **9** accounts for the observation of a Rh-H hydride (Eq. (6)). It is expected that **9**, like its methyl congener $(Ph_3P)_3Rh(Me)$, will undergo facile cyclometalation [5]. These observations and interpretation are summarized on the mechanistic description in Scheme 1.

This mechanism's rate law and the rate law from Eq. (7) would be mathematically equivalent when **2Cl** (or **1Cl**, depending on experimental conditions) is a non-steady state intermediate. However, one must exercise caution on assigning k_{obsd} and k'_{obsd} to specific mechanistic steps. For example, instead of the previous correlation where k_{obsd} and k'_{obsd} were associate to the set of consecutive reactions in Eq. (5), for reactions under flooding conditions ($[PPh_3]_{added} >> [\mathbf{1Cl}]_0$), k_{obsd} and k'_{obsd} are related to reactions in Scheme 1 by Eqs. (9) and (10), respectively.[4] It was observed that under flooding conditions where $[PPh_3]_{added} >> [\mathbf{1Cl}]_0$, k_{obsd} and k'_{obsd} are independent and dependent,