Available online at www.sciencedirect.com
ScienceDirect
Inorganica Chimica Acta 361 (2008) 3327–3331
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Note

Selective decarbonylation by a pincer PCP-rhodium(I) complex

Kuo-Wei Huang [a,*,1], David C. Grills [a], Joseph H. Han [b], David J. Szalda [c], Etsuko Fujita [a,*]

[a] *Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA*
[b] *Penguin Computing, 501 2nd Street, Ste 310, San Francisco, CA 94107, USA*
[c] *Department of Natural Sciences, Baruch College, New York, NY 10010, USA*

Received 30 November 2007; accepted 21 January 2008
Available online 8 February 2008

Dedicated to Professor Robert Angelici in recognition of his distinguished contributions to inorganic chemistry.

Abstract

Here we report a highly selective stoichiometric decarbonylation reaction for alkylformates and alkynyl aldehydes by a rhodium–dinitrogen complex (PCP-Rh–N_2) at room temperature. While electronic effects of the substrates cannot be completely ruled out, the selectivity is rationalized by a steric effect, consistent with the results of an X-ray crystallographic study and density functional theory (DFT) modeling.

Keywords: Selective decarbonylation; Steric effect; Pincer; Rhodium

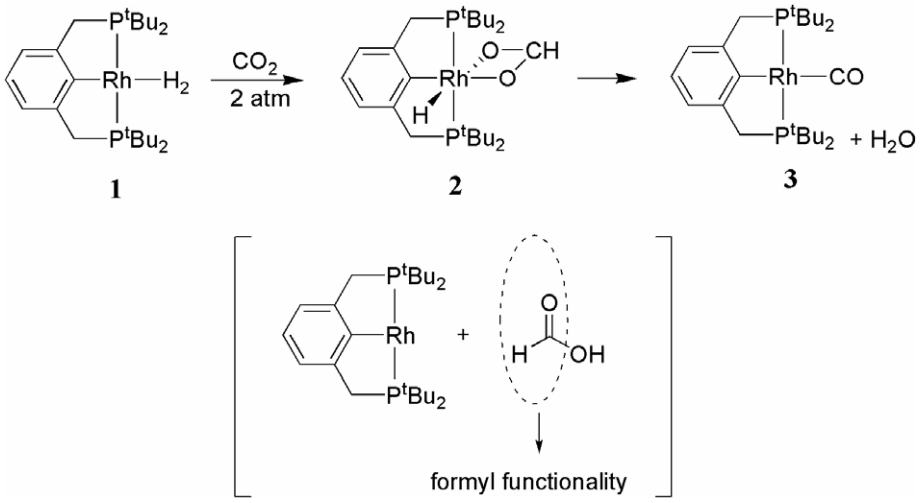
Rh(I) complexes have been employed for the decarbonylation of aldehydes and acyl and aroyl halides since the first demonstration by Tsuji and Ohno using Wilkinson's catalyst, $(PPh_3)_3RhCl$ [1–5]. While catalytic systems have been developed [6–10], due to several individual limitations, $(PPh_3)_3RhCl$ is still used as an efficient stoichiometric reagent for the decarbonylation of aldehydes in organic synthesis [11–13]. We have been investigating the mechanism of a unique Rh-mediated reverse water–gas shift (RWGS) reaction discovered by Kaska (Scheme 1) [14,15]. One of the important intermediates was identified as a hydridorhodium formate complex (**2**). Because of the general reactivity of Rh(I) complexes towards aldehyde decarbonylation, it was further proposed that complex **2** could undergo the reductive elimination of formic acid followed by a decarbonylation of the formyl functional group by the reduced PCP-Rh(I) center to generate the PCP-Rh–CO complex (**3**) as the final product. In an effort to support this proposed mechanism for the RWGS reaction and to explore the potential applications of pincer Rh(I) complexes as stoichiometric decarbonylation reagents, reactions of the model Rh(I) complex, PCP-Rh–N_2 (**4**), with formyl compounds were studied.

PCP-Rh–N_2 complex **4** was first treated with some common aldehydes (Table 1, entries 1–4), but to our disappointment, no reaction was observed.[2] Heating the reaction mixture at 50 °C in the case of *p*-tolualdehyde and 2-octenal for 6 h still resulted in no reaction. These results urged us to examine ethyl formate, a more chemically and structurally similar compound to formic acid, in the decarbonylation reaction study. In sharp contrast to the reactions with aldehyde substrates, the PCP-Rh–N_2 complex was found to react with ethyl formate quantitatively in time of mixing to give the PCP-Rh–CO complex (**3**) and ethanol at room temperature. These observations

* Corresponding authors. Tel.: +1 631 344 4356; fax: +1 631 344 5815.
E-mail addresses: hkw@nus.edu.sg (K.-W. Huang), fujita@bnl.gov (E. Fujita).
[1] Present address: Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore.

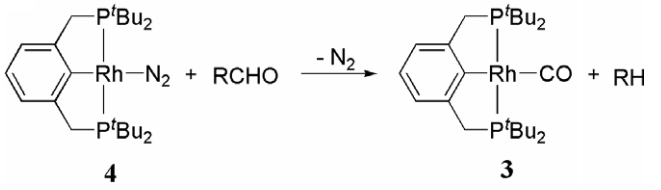
[2] *Representative procedure:* PCP-Rh–N_2 (**4**) (1.0 mg) was dissolved in 0.7 ml of benzene-d_6 and transferred into a 5 mm NMR tube capped with a white rubber septum in a nitrogen-filled glovebox. The aldehyde (1.2–1.5 equiv.) was added via a microsyringe at room temperature. The reaction was monitored by ^1H NMR on a 400 MHz Bruker Avance spectrometer.

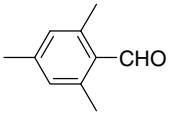
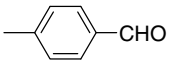
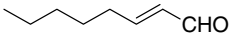
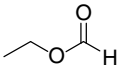
0020-1693/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2008.01.045



Scheme 1. Proposed intermediates for the Rh-mediated RWGS reaction.

Table 1
Reaction of PCP-Rh–N_2 (**4**) with RCHO[a]

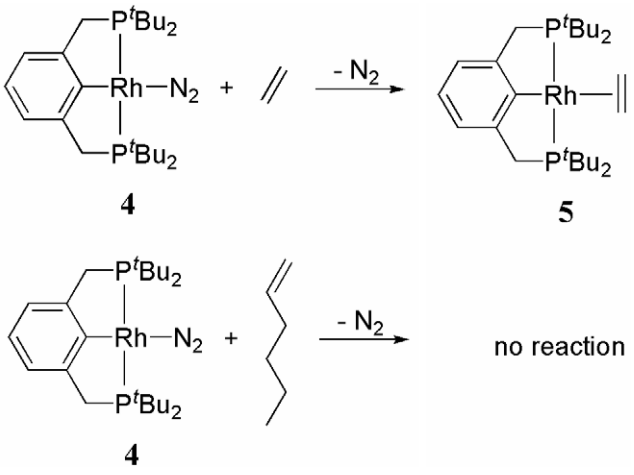


Entry	RCHO	Product
1		NR
2		NR
3		NR
4		NR
5		 [b]

[a] In benzene-d_6 solution at room temperature.
[b] Quantitative yield by ^{1}H NMR. NR = no reaction.

indicate that the decarbonylation reaction by **4** is extremely selective.

To assess the cause of this selectivity, olefin binding reactions to the PCP-Rh complex were studied, since the η^2-(C=O) bound species has been well-established as an important intermediate for the oxidative addition of the formyl C–H to the metal center, which is the first step involved in the decarbonylation reaction mechanism [16]. Upon treatment of **4** with ethylene, a ligand substitution led to the formation of the PCP-Rh–ethylene complex (**5**), consistent with the spectroscopic data in the literature [17]. Interestingly, when 1-hexene was used instead of ethylene, no reactivity towards the PCP-Rh–N_2 complex was detected at room temperature. This result implies that a steric effect might play an important role.



Support for the steric argument was further provided by an X-ray crystallographic study of complex **3** (Fig. 1, Table 2). Although **3** has been known for more than 30 years [18], no crystal structure has been obtained or reported until now. A pale yellow plate of **3** suitable for X-ray analysis was obtained from a hexane solution of **3** at −80 °C. The spacefilling model showed that the four bulky *t*-butyl groups create such a small "coordination cavity" that even the linear CO ligand can barely fit inside. In order to allow the decarbonylation of an aldehyde to occur, the formyl group has to reach the reduced metal center. It appears that the presence of the *t*-butyl groups may prevent the Rh center from being attacked by a large ligand.

The *A*-value, which is the energy difference between the equatorial and axial conformers of a mono-substituted cyclohexane, is one of the standard scales for comparison