

# Reactions of Silanes with Carbonyl Compounds Catalyzed by Rhenium and Manganese Carbonyl Complexes

Chun Keong Toh and Wai Yip Fan\*

<sup>1</sup>National University of Singapore, 3 Science Drive 3, Singapore 117543

\*chmfanwy@nus.edu.sg

## Introduction

Reductions of carbonyl compounds are usually done via hydride reductions using lithium aluminium hydride and sodium borohydride. However, such hydride compounds are very air and moisture sensitive. Recent studies on reduction of carbonyls using silanes via the process of hydrosilylation have been studied. The silanes used do not react with air and moisture and affords a cleaner reaction. Also, the hydrosilylation of aldehydes and ketones is a valuable transformation in organic synthesis because it generates protected alcohols in a single step. Such transformations are found to be catalyzed by tungsten<sup>1</sup>, ruthenium<sup>2</sup>, as well as activated forms of Rhenium complexes<sup>3</sup>.

In this work, we investigate the Si-H bond activation by  $\text{Re}(\text{CO})_5\text{Cl}$  and  $\text{Mn}(\text{CO})_5\text{Br}$  and their subsequent addition onto various carbonyl compounds like aldehydes, ketones, esters and carboxylic acids. To compare the reactivity of the various carbonyls towards hydrosilylation, additions to compounds containing 2 different carbonyl functional groups were also investigated. After which, mechanistic studies were also done to determine the active catalytic species.

## Experimental

All reactions involving  $\text{Mn}(\text{CO})_5\text{Br}$  were performed under atmospheric conditions whereas all reactions involving  $\text{Re}(\text{CO})_5\text{Br}$  were performed in vacuo using standard vacuum-line techniques. A typical hydrosilylation reaction involves the addition of the Rhenium complex with the carbonyl and silane under neat conditions, into a Quartz tube. The solutions were laser irradiated using a Legrand Broadband Lamp (200-800nm, 11W), and stirred at room temperature for 4 hours.

IR spectra of the catalytic intermediates were recorded with a Shimadzu IR Prestige-21 Fourier-Transform IR spectrometer (1000–4000  $\text{cm}^{-1}$ , 1  $\text{cm}^{-1}$  resolution, 8 scans co-added for spectral averaging) using a 0.05 mm pathlength calcium fluoride cell. <sup>1</sup>H-NMR spectra were recorded in  $\text{CDCl}_3$  on a Bruker AV 500 Fourier-Transform spectrometer operating at ca. 500 MHz. The

chemical shifts were reported relative to TMS. Mass spectra of the hydrosilylated products were recorded with a Finnigan Mat 95XL-T spectrometer.

## Results/Discussion

All hydrosilylation reactions afforded the resultant silylether or silylester with more than 70% yield and siloxanes as the side product. Interestingly, hydrosilylation with esters such as ethyl acetate also afforded aldehydes (ethanal in the case of ethyl acetate) as side products. <sup>1</sup>H-NMR and EI-MS have been used to confirm the identities of the organic products.

Reactions with compounds containing two different carbonyl functional groups show that acids and aldehydes afforded comparable yields in the same reaction time. The reactivities of the various carbonyls are as follows: Carboxylic Acid, Aldehydes > Ketones > Esters.

It was found that  $\text{Mn}(\text{CO})_5\text{Br}$  was able to effect the hydrosilylation of carbonyls with comparable yields to that of  $\text{Re}(\text{CO})_5\text{Cl}$  without any photolytic irradiation under atmospheric conditions. However, mechanistic studies were difficult as the Manganese-Silyl intermediate was very unstable.

Mechanistic studies were done using  $\text{Re}(\text{CO})_5\text{Br}$  instead and it was found that the active catalytic species was the  $\text{Re}(\text{CO})_5\text{H}$  species.

## References.

1. Gadek, A.; Szymanska-Buzar, T. *Polyhedron*, 2006, 25, 1441
2. Hanada, S.; Ishida, T.; Motoyama, Y.; Nagashima, H. *J. Org. Chem.* 2007, 72, 7551
3. Dong, H.; Berke, H.; *Adv. Synth. Catal.* 2009, 351, 1783