

# Accepted Manuscript

Adducts of Mn and Re vinylidenes with P–OR nucleophiles: Hydrolysis rather than the intramolecular Michaelis–Arbuzov rearrangement

Kamil I. Utegenov, Vasily V. Krivykh, Oleg S. Chudin, Alexander F. Smol'yakov, Fedor M. Dolgushin, Oleg V. Semeikin, Nikolai A. Shteltser, Nikolai A. Ustynyuk



PII: S0022-328X(17)30584-3

DOI: [10.1016/j.jorganchem.2017.10.008](https://doi.org/10.1016/j.jorganchem.2017.10.008)

Reference: JOM 20128

To appear in: *Journal of Organometallic Chemistry*

Received Date: 22 August 2017

Revised Date: 6 October 2017

Accepted Date: 10 October 2017

Please cite this article as: K.I. Utegenov, V.V. Krivykh, O.S. Chudin, A.F. Smol'yakov, F.M. Dolgushin, O.V. Semeikin, N.A. Shteltser, N.A. Ustynyuk, Adducts of Mn and Re vinylidenes with P–OR nucleophiles: Hydrolysis rather than the intramolecular Michaelis–Arbuzov rearrangement, *Journal of Organometallic Chemistry* (2017), doi: 10.1016/j.jorganchem.2017.10.008.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

# Adducts of Mn and Re Vinylidenes with P–OR Nucleophiles: Hydrolysis rather than the Intramolecular Michaelis–Arbuzov Rearrangement<sup>#</sup>

Kamil I. Utegenov,<sup>a</sup> Vasily V. Krivykh,<sup>a,\*</sup> Oleg S. Chudin,<sup>b</sup> Alexander F. Smol'yakov,<sup>a,c</sup> Fedor M. Dolgushin,<sup>a</sup> Oleg V. Semeikin,<sup>a</sup> Nikolai A. Shteltser,<sup>a</sup> and Nikolai A. Ustynyuk<sup>a,\*</sup>

<sup>#</sup>The authors dedicate this paper to Prof. Irina P. Beletskaya, a famous expert in organometallic chemistry and catalysis.

<sup>a</sup> A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russian Federation

<sup>b</sup> Institute of Chemistry and Chemical Technology, Siberian Branch of the Russian Academy of Sciences, ul. K. Marksa 42, Krasnoyarsk, 660049 Russian Federation

<sup>c</sup> Faculty of Science, RUDN University, ul. Miklukho-Maklaya 6, Moscow, 117198 Russian Federation

\* Corresponding author. E-mail address: [ustynyuk@ineos.ac.ru](mailto:ustynyuk@ineos.ac.ru), [ykriv@ineos.ac.ru](mailto:ykriv@ineos.ac.ru)

## Abstract

The reactions of vinylidene complexes  $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}=\text{C}(\text{H})\text{Ph}$  (**Mn1**) and  $\text{Cp}(\text{CO})_2\text{Re}=\text{C}=\text{C}(\text{H})\text{Ph}$  (**Re1**) with P–OR nucleophiles  $\text{P}(\text{OR})\text{R}'\text{R}''$  ( $\text{OR} = \text{R}' = \text{R}'' = \text{OMe}$ ,  $\text{OEt}$ ,  $\text{OPr}^i$ ,  $\text{OPh}$ ;  $\text{OR} = \text{OEt}$ ,  $\text{R}' = \text{R}'' = \text{Ph}$ ;  $\text{OR} = \text{R}' = \text{OEt}$ ,  $\text{R}'' = \text{Ph}$ ) proceed as nucleophilic addition to the  $\text{C}_\alpha$  vinylidene atom to initially afford zwitter-ionic complexes  $\text{Z-Cp}(\text{CO})_2\text{M}^- - \text{C}^+[\text{P}(\text{OR})\text{R}'\text{R}''] = \text{C}(\text{H})\text{Ph}$  which were identified by spectroscopic methods and, in some cases, their molecular structures were confirmed by X-ray diffraction. These adducts are extremely sensitive to water and hydrolyzed by water traces to afford the corresponding  $\eta^2$ -phosphorylalkene complexes  $\text{Cp}(\text{CO})_2\text{M}\{\eta^2\text{-E-HC}[\text{P}(\text{O})\text{R}'\text{R}'']=\text{C}(\text{H})\text{Ph}\}$ . The isotopic label experiments with  $\text{D}_2\text{O}$  and  $\text{H}_2^{18}\text{O}$  showed the hydrolysis to proceed with the phosphorus–oxygen bond cleavage and binding of the water hydrogen to the carbon atom bearing the  $>\text{P}=\text{O}$  group.

**Keywords:** transition metal vinylidenes, manganese complexes, rhenium complexes, alkenylphosphonate complexes, phosphites, quasiphosphonium cations.

## 1. Introduction

The Michaelis–Arbuzov reaction (hereinafter referred to as the MA reaction) is one of the universal and well-studied tools for the formation of carbon–phosphorus bonds [1,2]. It is widely used primarily for the synthesis of phosphonates, phosphinates, and phosphine oxides, but also

Download English Version:

<https://daneshyari.com/en/article/7755857>

Download Persian Version:

<https://daneshyari.com/article/7755857>

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