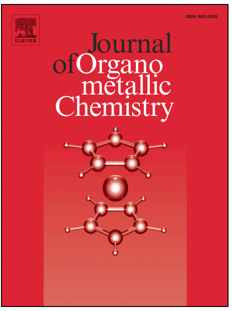

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Adducts of Mn and Re Vinylidenes with P–OR Nucleophiles: Hydrolysis rather than the Intramolecular Michaelis–Arbuzov Rearrangement[#]

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[#]The authors dedicate this paper to Prof. Irina P. Beletskaya, a famous expert in organometallic chemistry and catalysis.

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Abstract

The reactions of vinylidene complexes $Cp(CO)_2Mn{=}C{=}C(H)Ph$ (**Mn1**) and $Cp(CO)_2Re{=}C{=}C(H)Ph$ (**Re1**) with P–OR nucleophiles P(OR)R'R" (OR = R' = R" = OMe, OEt, OPr^i, OPh; OR = OEt, R' = R" = Ph; OR = R' = OEt, R" = Ph) proceed as nucleophilic addition to the C_α vinylidene atom to initially afford zwitter-ionic complexes *Z*-$Cp(CO)_2M^{-}{-}C[^{+}P(OR)R'R'']{=}C(H)Ph$ 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 η^2-phosphorylalkene complexes $Cp(CO)_2M\{\eta^2\text{-}E\text{-}HC[P(O)R'R'']{=}C(H)Ph\}$. The isotopic label experiments with D_2O and $H_2{}^{18}O$ showed the hydrolysis to proceed with the phosphorus–oxygen bond cleavage and binding of the water hydrogen to the carbon atom bearing the >P=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