

CH activations in aldehydes in reactions with $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{15}^{\star}$ Richard D. Adams^{*}, Humaiara Akter, Jonathan D. Tedder

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ABSTRACT

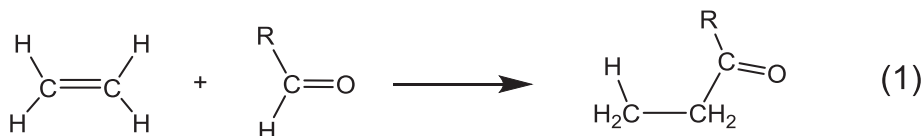
The reaction of $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{15}$, **1** with benzaldehyde yielded two new pentaruthenium carbido cluster compounds: $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{14}[\eta^2\text{-O=C(H)C}_6\text{H}_4](\mu\text{-H})$, **2** and $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{14}(\mu\text{-}\eta^2\text{-O=CPh})(\mu\text{-H})$, **3** containing open Ru_5C cluster complexes formed by the activation of two different C-H bonds of the benzaldehyde molecule. Compound **2** contains a chelating, ortho-metallated benzaldehyde ligand coordinated to an open Ru_5C cluster that is coordinated by the aldehyde oxygen atom and one of the ortho-positioned carbon atoms of the phenyl ring that was formed by loss of a CO ligand and an oxidative addition of the ortho-C-H bond of the phenyl ring to the metal atom. Compound **3** is an isomer of **2** that contains an O=C-coordinated, η^2 -bridging benzoyl ligand across the open edge of the Ru_5C cluster formed by C-H activation at the aldehyde formyl group. The reaction of **1** with trans-cinnamaldehyde yielded two complexes: $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{14}[\eta^2\text{-O=C(H)CH=CPh}](\mu\text{-H})$, **4** and $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{14}[\mu\text{-}\eta^2\text{-O=CC(H)=C(H)Ph}](\mu\text{-H})$, **5**. Compound **4** contains an open Ru_5 cluster with a chelating cinnamoyl ligand formed by coordination of the aldehyde oxygen atom and the β -carbon atom of the alkene double bond formed by a C-H activation at the alkene atom. Compound **5** contains a η^2 -bridging, O=C coordinated cinnamoyl group formed by C-H activation at the aldehyde formyl group. The reactions of **1** with furfural and 5-hydroxymethylfurfural yielded similar complexes: $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{14}(\mu\text{-}\eta^2\text{-O=CC}_4\text{OH}_3)(\mu\text{-H})$, **6** and $\text{Ru}_5(\mu_5\text{-C})(\text{CO})_{14}[\mu\text{-}\eta^2\text{-O=CC}_4\text{OH}_2(\text{CH}_2\text{OH})](\mu\text{-H})$, **7**, respectively with each one containing bridging, O=C coordinated acyl ligand formed by C-H activation at the aldehyde formyl group. All of the new compounds were characterized by single-crystal X-ray diffraction analyses.

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1. Introduction

The ability to activate and functionalize C-H bonds in hydrocarbons to produce higher-value organic chemicals is of great importance to the chemical industry. Accordingly, the activation and functionalization of C-H bonds by metal complexes has

received considerable research attention in recent years. Most studies have been focused on the activation of aliphatic [1] and aromatic [2] C-H bonds. The activation of aldehydic C-H bonds has also received considerable attention and is a key step in reactions known generally as the hydroacylation of alkenes and alkynes that are catalyzed by transition metal complexes (eq. (1)) [3].



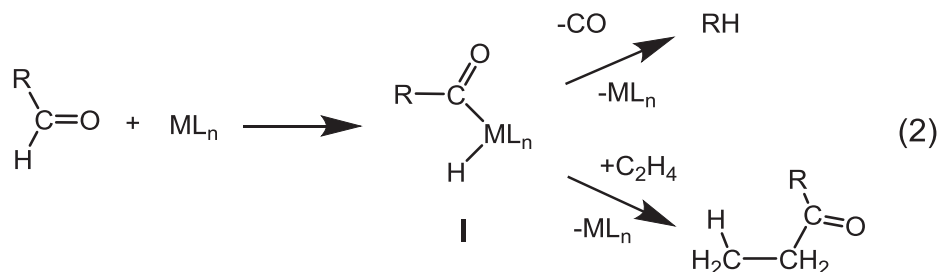
The oxidative addition of aldehydic C-H bonds to a metal complex will yield a metal complex **I** containing acyl and hydrido ligands that can undergo further transformations such as decarbonylation with subsequent formation of C-H bonds to yield a RH product by reductive elimination [4], or by coupling with an

^{*} Dedicated to Professor Richard J. Puddephatt for his many pioneering contributions to the field of organometallic chemistry on the occasion of his 75th birthday.

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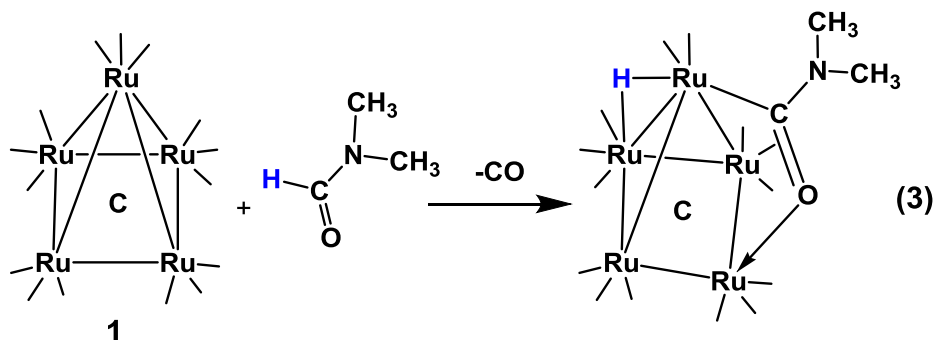
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unsaturated substrate, e. g. C_2H_4 , to yield a ketone by hydroacylation [5], (eq. (2)).



The competing decarbonylation process can significantly limit the usefulness of the more valuable hydroacylation reaction.

In recent studies, we have shown that the pentaruthenium cluster complex $Ru_5(\mu_5-C)(CO)_{15}$, **1**, is able to activate the formyl C-H bond of *N,N*-dimethylformamide to yield the complex $Ru_5(\mu_5-C)(CO)_{14}(\mu-\eta^2-O=CN(CH_3)_2)(\mu-H)$ that contains a bridging formamido $\eta^2-O=CN(CH_3)_2$ ligand formed by opening of the Ru_5C square pyramid cluster of metal atoms via oxidative addition of the formyl C-H bond, eq. (3) [6].



We have now investigated the reactions of **1** with a series of selected aldehydes: benzaldehyde, cinnamaldehyde, furfural and 5-hydroxymethylfurfural, and have observed some similar cluster opening C-H bond activations at the formyl functional groups and in some cases C-H activations on neighboring aryl and olefinic substituents. Herein we report on our new studies of the activation of aldehydic C-H bonds by the cluster complex **1**.

2. Experimental section

2.1. General data

All reactions were performed under an atmosphere of nitrogen. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Thermo Scientific Nicolet IS10. 1H NMR spectra was recorded on a Varian Mercury 300 spectrometer operating at 300.1 MHz. Mass spectrometric (MS) measurements were performed by a direct-exposure probe by using electron impact (EI) ionization. $Ru_3(CO)_{12}$ was obtained from STREM and was used without further purification. $Ru_5(\mu_5-C)(CO)_{15}$, **1** was prepared from $Ru_3(CO)_{12}$ according to a previously reported procedure [7]. Benzaldehyde,

C_6H_5CHO , was obtained from Sigma-Aldrich and was purified by trap-to-trap distillation techniques prior to use. Trans-cinnamal

dehyde, $C_6H_5CH=CHCHO$, furfural and 5-hydroxymethyl-2-furaldehyde (5-hydroxymethylfurfural) were obtained from Sigma Aldrich and were used without any further purification. Product separations were performed by TLC in air on Analtech 0.25 mm and 0.50 mm silica gel 60 Å F254 glass plates and silica gel column chromatography on silica gel 60, 0.606–0.2 mm (70–230 mesh).

2.2. Reaction of $Ru_5(\mu_5-C)(CO)_{15}$, **1** with benzaldehyde at 98 °C

49.9 mg (0.053 mmol) of **1** was added to a 50 mL three-neck flask with a solution of 30 μ L of benzaldehyde in 20 mL of degassed heptane. After heating for 13 h at 98 °C, the solvent was removed *in vacuo*, and the products were then isolated by TLC by using a hexane/methylene chloride solvent mixture to provide in order of elution: 2.7 mg of $Ru_5(\mu_5-C)(CO)_{14}[\eta^2-O=C(H)C_6H_4](\mu-H)$, **2** (5% yield), and 22.3 mg of $Ru_5(\mu_5-C)(CO)_{14}(\mu-\eta^2-O=CPh)(\mu-H)$, **3** (41% yield). Spectral data for **2**: IR ν_{CO} (cm^{-1} in hexane): 2096(w), 2066(s), 2056(vs), 2048(m), 2034(w), 2022(w), 2018(sh), 2013(sh), 1995(w), 1989(w), 1974(vw). 1H NMR (CD_2Cl_2 , in ppm) δ = 9.28 (s, 1H, C(H)=O), 8.37 (d, $^3J_{H-H}$ = 8 Hz, 1H, CH(CH)₂CH), 8.00 (d, $^3J_{H-H}$ = 8 Hz, 1H, CH(CH)₂CH), 7.55 (t, $^3J_{H-H}$ = 7 Hz, 1H, CH(CH)₂CH), 7.30 (t, $^3J_{H-H}$ = 7 Hz, 1H, CH(CH)₂CH), -22.36 (s, 1H, hydride). EI/MS *m/z*. 1015. The isotope distribution pattern is consistent with the presence of five ruthenium atoms. Spectral data for **3**: IR ν_{CO} (cm^{-1} in hexane): 2105(w), 2077(s), 2060(vs), 2053(m), 2033(m), 2017(m), 2012(sh), 2003(w), 1993(w), 1972(w). 1H NMR (CD_2Cl_2 , in ppm) δ = 7.46–7.29 (m, 5H, O=C(C₆H₅)), -20.96 (s, 1H, hydride). EI/MS *m/z*. 1015. The isotope distribution pattern is consistent with the presence of five ruthenium atoms. Note: There was no evidence of a reaction between benzaldehyde and compound **1** at room temperature by IR or 1H NMR spectroscopy.

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