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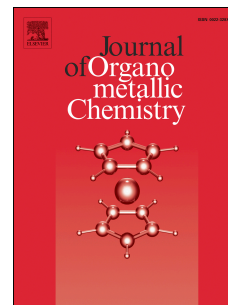
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Oxidation of olefins catalyzed by half-sandwich osmium(II) arene complexes

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Abstract

Ten complexes $[(\eta^6\text{-arene})\text{OsCl}(\text{C}_5\text{H}_4\text{N-2-CH=N-C}_6\text{H}_5\text{X})]\text{PF}_6$ (with arene = *p*-cymene (**1**) or benzene (**2**); X = 4-F (**a**), 4-Cl (**b**), 4-Br (**c**), 4-I(**d**) and 4-methyl (**e**)) were synthesized by reacting the corresponding N,N'-bidentate ligands with the osmium arene dimers $[(\eta^6\text{-arene})\text{Os}(\mu\text{-Cl})\text{Cl}]_2$ in a 2:1 ratio. Complexes **1a-e** and **2c-d** are new. The compounds were fully characterized via ^1H and ^{13}C NMR, IR and UV-Vis spectroscopy, and elemental analyses. The x-ray crystal structure of compound **2e** is also reported. The Os(II) complex shows the expected “piano stool” type geometry. These Os(II) compounds were investigated in the catalytic oxidation of olefins to carbonyl compounds with NaIO_4 as terminal oxidant in a $\text{H}_2\text{O}/t\text{-BuOH}$ biphasic system. All of the compounds were very effective catalysts for this reaction and gave the corresponding aldehyde in high yields.

Key words: Osmium; N,N'-bidentate ligands; arene; styrene oxidation; olefin oxidation; x-ray structure

1. Introduction

The oxidative cleavage of alkenes to give the corresponding aldehydes, ketones or acids is a very important transformation in organic synthesis [1]. There are two main oxidative pathways discussed in literature for this oxidative cleavage [2]; the first pathway involves the oxidation of the alkenes into 1,2-diols which is followed by cleavage with NaIO_4 or other oxidants. The second route involves ozonolysis where the alkene is cleaved into a number of possible functionalized products, which depend on the workup conditions [2]. Ozonolysis is the standard method; however, it needs to be very carefully controlled due to the risk of explosion. Therefore, alternate reactions for the direct cleavage of alkenes, some without 1,2-diol intermediates, are

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