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Additive Free Isomerization of Allylic Alcohols to Ketones with 1st Row Transition Metal PNP Pincer Catalysts

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PURPOSE OF THE ABSTRACT

Isomerization reactions are receiving a growing interest since they lead to transfunctionalization of a variety of organic compounds according to Green Chemistry principles.[1] It is of a high interest to investigate catalysts which convert allylic alcohols into saturated carbonyl compounds. During the last half century precious metal catalysts, such as Ir, Ru, Rh or Pd have been mainly used for this purpose.[2] Notwithstanding the importance of such catalytic systems, they are based on expensive and rare elements. By comparison, most of the first-row transition metals are inexpensive, earth-abundant and more benign.[3] Recently, pincer complexes of 1st row transition metals have been discovered to be effective catalysts for hydrogenation, dehydrogenation, transfer hydrogenation, alkylation and olefin isomerization reactions.[4]

Herein, we report the isomerization of allylic alcohols to ketones in the presence of Fe,[5] Mn and Co pincer complexes. Mechanistic studies were performed for this transformation, where it was found, that the Fe- and Mn-catalysts operate via dehydrogenation / hydrogenation mechanism. The current results suggest that the Co catalysts operate via a metal hydride, where classical isomerization occurs, while a dehydrogenation / hydrogenation mechanism also takes place at the same time.

FIGURES

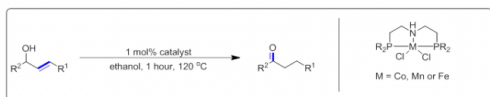


FIGURE 1

Isomerisation of allylic alcohols to ketones

Scheme 1

FIGURE 2

KEYWORDS

Isomerisation | Iron | Cobalt | Pincer

BIBLIOGRAPHY