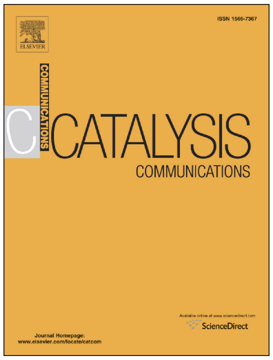

A computational study of structures and catalytic activities of Hoveyda-Grubbs analogues bearing coumarin or isopropoxycoumarin moiety

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Title: A computational study of structures and catalytic activities of Hoveyda-Grubbs analogues bearing coumarin or isopropoxycoumarin moiety

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Abstract:

The DFT/M06-D3 method was used to investigate structures and activation free energies for a series of Hoveyda-Grubbs-like catalysts with the isopropoxybenzene part replaced by coumarin (2H-chromen-2-one) and ten derivatives of isopropoxycoumarin. Out of ten investigated isopropoxycoumarin derivatives two show free enthalpies of initiation around 3-5 kcal/mol lower than the Hoveyda-Grubbs catalyst and free enthalpies of the catalytic cycle around 2-3 kcal/mol lower than the Hoveyda-Grubbs suggesting fast initiation. Additionally, correlations between the initiation free enthalpies and ruthenium-oxygen bond strengths as well as natural partial charges on carbene carbon atom have been found, described and rationalized.

Keywords: DFT; olefin metathesis; ruthenium; Hoveyda-Grubbs catalyst; coumarins

1. Introduction

The possibility of controlled synthesis of new carbon-carbon bonds to transform simple molecules to more complex ones has been a major area of research in organic chemistry since decades. One of the most commonly used reactions used for this purpose is the olefin metathesis, which includes reorganization of pairs of carbon-carbon double bonds [1,2]. The second generation Hoveyda-Grubbs catalyst **1** was one of the first efficient, phosphine-free ruthenium-based catalysts which is still widely used today [3,4]. More importantly there are numerous examples of miscellaneous derivatives of this complex which alter its electronic properties and catalytic activity [5-7]. The benzylidene part of the Hoveyda-Grubbs catalyst catalysts is particularly interesting in this context, as it can be relatively easy modified. One notable example was the modification of the isopropoxybenzene part of Hoveyda-Grubbs catalyst into 2,3-dihydrobenzofuran (**2**) or chromane (**3)** moiety (see Fig. 1) [8]. Authors argued, that in such complexes the crucial Ru-O distance will be higher than in the parent Hoveyda-Grubbs catalyst resulting in easier Ru-O bond dissociation and faster initiation of the catalyst. The 2,3-dihydrobenzofuran-substituted catalyst has not been, unfortunately, isolated, but the chromane-substituted catalyst showed indeed fast initiation, on the level of the fast Grela nitro catalyst. A different study has shown that several other benzofuran derivatives-substituted catalyst (**4**,**5**) were not stable [9]. We have later shown computationally that benzofuran-substituted catalyst **6** is likely to be unstable due to a relatively weak Ru-O interaction [10]. The general conclusion from these studies is that due to geometrical constraints the oxygen atom of the five-membered benzofuran ring is positioned too far from the ruthenium center to provide sufficient coordination, yielding an unstable precatalyst.