



Research Paper

Metal-catalyzed rearrangement of allenylsulfides to furan: A theoretical mechanistic approach

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ARTICLE INFO

Article history:

Received 12 July 2017

Received in revised form

25 September 2017

Accepted 27 September 2017

Keywords:

Molecular mechanism

Homogeneous catalysis

Transition metals

Cyclization

Allenyls

Density functional calculations

ABSTRACT

A furan catalytic synthesis from allene is studied with quantum chemistry computations. Both specific and non-specific solvent effect are considered. The complete catalytic cycle is studied for three metals, and compared to experimental data. The mechanism is disclosed and the catalyst regeneration shows clear difference between the three metals. For Pt, the regeneration corresponds to a two-steps mechanism with a stable intermediate. For Au and Ru catalysts the regeneration is a one step mechanism with a low barrier only for Au (3.8 kcal/mol). For Au, the results of the computations contrasts with the experiments, hence a poisoning of the catalyst is most likely. On the contrary, in the Ru case, the regeneration corresponds to the highest transition state of the cycle.

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1. Introduction

Allenyls have attracted significant attentions as a consequence of their unique structural feature and chemical reactivities [1–11]. The allenyl moieties can coordinate with transition-metals, thus being activated. The activated allenyl moieties are prone to be attacked by nucleophiles, and subsequently various transformations that are highly useful in organic synthesis can be triggered. In particular, the transition-metal-catalyzed reaction of allenyls bearing α -substituents as internal nucleophiles makes it possible to develop efficient synthetic method for heterocycles. One of such transformations is the transition-metal-catalyzed cyclization of allenyl ketones that affords furans in a straightforward manner (Fig. 1) [12–17]. Several metals are found in the literature as useful catalysts for this purpose. The catalyst can be for instance a calcium complex [18–20], but electron-rich metals such as gold, platinum, and ruthenium are also used. The reaction is a cycloisomerisation with atoms or even groups transpositions [21–23].

Furans are important heterocycles, which are present as key structure units in many biologically important natural products and pharmaceutical substances [24]. Furans are also widely used

as building blocks in organic synthesis [25]. Thus, the development of novel and efficient approach to furan derivatives has been an active research area over the years [26–34]. One of the authors previously studied the transition metal-catalyzed reaction of allenyl sulfides. The reaction proceeds through an intriguing 1,4-migration of thio group to afford furan derivatives, as shown in Fig. 1 [35]. The reaction presumably involves a metal carbene intermediate, which is trapped intramolecularly by carbonyl group. To gain detailed insights into the reaction mechanism of this novel transformation, we have launched a computational study on this reaction.

Indeed, in the present contribution, we address the mechanism of this catalysis by computing the different intermediates and transition states summarized in Fig. 2. Three **MLn** catalysts are studied AuCl, PtCl₂ and {RuCl₂(*p*-cymene)}. They correspond to the catalysts experimentally studied for this reaction, as reminded in Table 1. We shall thus refer explicitly to experimental results in the discussion.

Moreover, for each catalyst, a special attention will be given to the step that concerns the catalyst regeneration. Notably, the aforementioned C¹ → C⁴ migration involves two ring closures and one ring opening. The postulated cyclic intermediate is named here **S-Cycle**: we use for the name the label of heteroatom that closes the ring. A **Carbenoid** intermediate is then postulated, and upon the C³-O bond formation, it connects to the complex formed by the furan (reaction product) and the catalyst. We refer to this complex

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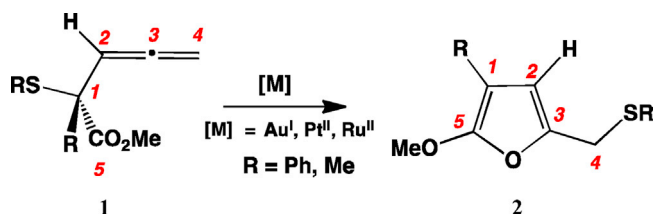


Fig. 1. Cycloisomerisation-transposition at work. Experimentally, Phenyls are used as R substituents. Methyls are used in computations.

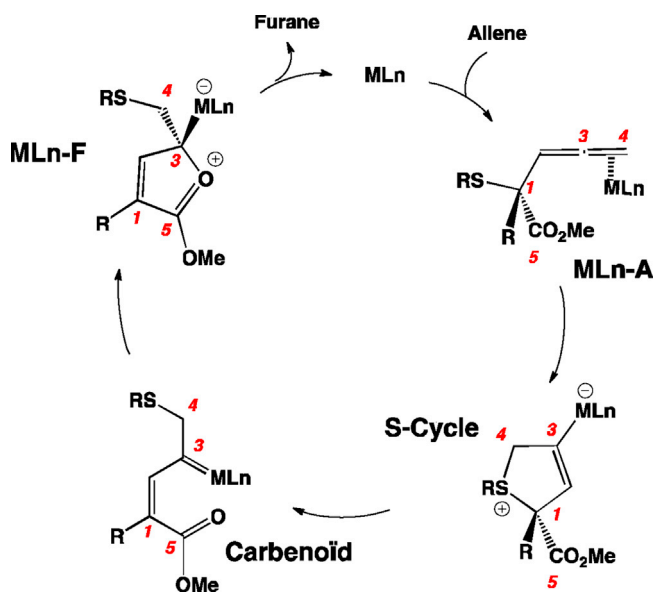


Fig. 2. Catalytic cycle proposed for the cycloisomerisation-transposition; adapted from ref [35]. Experimentally, phenyls are used as R substituents. In computations methyls are used instead.

with the label **MLn-F**. The so-called **MLn** catalyst is then restored upon **Furan – Allene** exchange.

2. Methods

The computations were done at the level M06-D3/lanl2dz(d), and we accounted for non specific solvent effects of the toluene with the standard PCM method. Specific effects were handled with one benzene molecule explicitly introduced on the metal: **MLn** refers to the complex with the benzene ligand. The reaction described in Fig. 1 is exothermic by -24.4 kcal/mol (when R = Phenyl). In order to alleviate the computations, we modeled the R = Phenyl substituent by R = Methyl throughout. With R = Methyl, the reaction exothermicity is smaller (-16.5 kcal/mol). Such a difference is due to the conjugation of the R = Phenyl with the double bond $C^1 = C^5$ formed in the product (Fig. 1). Indeed, the R = Methyl does not conjugate, so the exothermicity is smaller in the model. Hence, the choice of this model will alter the energetics of the reaction mechanism whenever the R substituent conjugates with double bonds: the **Carbenoid**, and the **MLn-F** intermediates would be about 7 kcal. mol^{-1} lower when R = Phenyl compared to the model computations. We shall be watchful on that. A second simplification concerns the Ru catalyst: the *p*-cymene was modeled with a phenyl. This was done to limit the number of possible orientations of this ligand and as *a priori* no effect on the energetics. Our computations were done with the Gaussian g09 D01 suite of programs [36], and the non specific solvent effect was modeled with the IEF-PCM solvation model [37], as implemented in Gaussian. The M06/lanl2dz(d) level of calculation was used throughout,

Table 1
Main experimental results from ref [35].

Catalyst ^[a]	T[°C]	t[h]	Yield[%] ^[b]
AuCl	80	17	Trace ^[c]
PtCl ₂	80	4.5	73
{RuCl ₂ (<i>p</i> -cymene)}	80	1	93
{RuCl ₂ (<i>p</i> -cymene)}	25	23	88

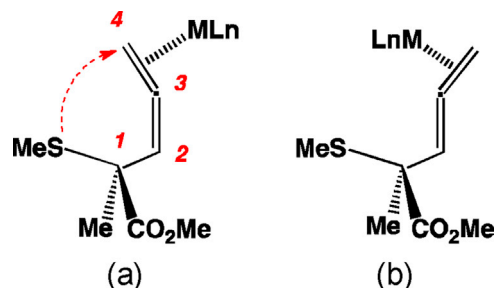


Fig. 3. The interaction with the metal leads to two possible complexes.

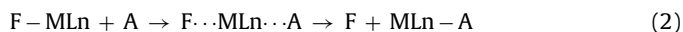
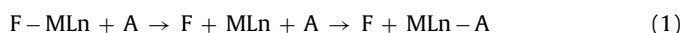
and this M06 level [38–40] was supplemented with Grimme's long range dispersion correction D3 [41–44]. The (d) in the lanl2dz(d) acronym corresponds to polarization function that we added to the standard relativistic ECP and basis set lanl2dz [45]. The 3d polarization functions concerned the 3d orbitals of Carbon and Oxygen with exponents $\zeta_{dC} = 0.75$ and $\zeta_{dO} = 0.85$. These values come from the exponent of the D95(d) (or DZP) basis set, as implement in Gaussian. Our computations used the chain method (**CHAIN**) [46,47] and AMPAC [48] to find the best paths that link **MLn-A** reactive to the product **MLn-F**. More details on the structures can be found in the experimental section. Additionally, several other paths and all the structures are available in the Supplementary material (29 pages).

2.1. Metal – allene complexes: MLn-A tables

In the first step of the reaction, the metal has to bind to the allene. Upon the formation of the complex, the allene loses its quasi linearity, and bends at the central C^3 atom with an angle of about 160° [49–54]. The stabilization is of 10.1, 34.6 and 12.2 kcal mol^{-1} for the Au, Pt and Ru catalysts, respectively. Two orientations can be found, with the metal either exo- to the thiolate (a), or endo- (b). These two situations are reminded in Fig. 3. It is noteworthy that the (a) situation allows a direct 1,4 migration of the thiolate group. The endo- orientation was also studied, and we showed that this path does not correspond to effective intermediates. A detailed study is included in the supplementary material.

2.2. Catalyst regeneration: furane – metal – allene complexes

Once the furane is formed, the catalyst has formed, F-MLn contains a metal–Carbon bond that needs to break in order to renew the catalyst and allow a new allene molecule to come in the cycle. This can be achieved through either a dissociative (Eq. (1)) or an associative path (Eq. (2)). However, the dissociation of the furane from the catalyst costs at least 14.6 kcal/mol (for Au, Ru), and up to 38.9 kcal/mol (Pt case). On the other hand, the approach of the allene involves at first stabilizing interactions. Finally, the associative path is always lower in energy than the dissociative.



As we shall see, this Furane – Allene exchange that completes the catalytic cycle is of primary importance, and each catalyst behave differently also for this matter. For consistency in the energetics, the

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