Journal of Catalysis 364 (2018) 345–353

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

An unexpected formation of a Ru(III) benzylidene complex during activation of a LatMet-type ring-opening polymerisation catalyst ☆

Anna Gawin [a,1], Paweł Małecki [a], Maciej Dranka [b], Janusz Zachara [b], Magdalena Skompska [a,c,*], Anna Kajetanowicz [a,*], Karol Grela [a,*]

[a] Biological and Chemical Research Centre, Faculty of Chemistry, University of Warsaw, Żwirki i Wigury Street 101, 02-089 Warsaw, Poland
[b] Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland
[c] Laboratory of Electrochemistry, Faculty of Chemistry, University of Warsaw, Pasteur 1, 02-093 Warsaw, Poland

A R T I C L E   I N F O

Article history:
Received 7 March 2018
Revised 6 May 2018
Accepted 14 May 2018

Keywords:
Ru(III)
Olefin metathesis
DCPD
ROMP
RCM

A B S T R A C T

Upon activation with C_2Cl_6 known latent Ru metathesis catalyst LatMet (**13**) exhibited activity in RCM and in ROMP of DCPD. A by-product of such activation, an aryloxybenzylidene ruthenium(III) complex **17** have been independently synthesised by reacting **13** with C_2Cl_6. This unique complex was characterised by spectroscopic and electrochemical methods, and by X-ray crystallography. To the best to our knowledge, this is the first isolated and structurally determined Ru(III) alkylidene complex reported.

1. Introduction

Catalytic olefin metathesis has become a powerful tool for the formation of carbon–carbon bonds in organic and polymer chemistry [1]. The latter can be considered as one of the most rapidly growing industrial application of the metathesis technology, both from the point of view of production tonnage, but also from the point of view of its business value [2]. From numerous types of metathesis-based polymerisation processes known [3], the ring opening metathesis polymerisation (ROMP) of dicyclopentadiene (DCPD) assures a special attention [4] as the formed polymer can be easily processed into durable composite materials ideally suited for extreme environments. It shall be noted that Polydicyclopentadiene (PDCPD) exhibits a number of unique chemical and physical properties, such as low water absorption, high thermal and chemical corrosion resistance, high impact strength and resistance to crack propagation. Therefore ROMP of DCPD provides new perspectives for oil and gas drilling (e.g. deep water pipeline insulation materials), transportation, energy production, and other industries. From the point of view of Carbon Footprint, it was claimed that modern PDCPD-based materials, such as Materia's Proxima® Thermoset Resins can have up to 50% lower cradle-to-gate emissions [5].

However, to make ROMP of DCPD adaptable to industry-standard manufacturing processes, such as RIM (Reaction Injection Moulding), the polymerisation process must be precisely controlled and the monomer/initiator composition stable over time. Unfortunately, the most of general-purpose catalysts (selected structures are shown in the first row of Fig. 1) do not give good results in ROMP of such reactive monomer, especially when industrial scale is considered [6]. To solve this problem, a number of so-called "latent" or "dormant" Ru-catalysts have been developed in recent years [7]. The use of such catalysts in ROMP allows for the catalyst to be mixed with the monomer with no or only little polymerization, in order to give enough time to handle the formulation. Once required, the catalyst can be activated by chemical or physical methods, such as acids (HCl, TMSCl), heat, or light [8]. Selected Ru catalysts that amply fulfil these prerequisites, and have been successfully used in ROMP of DCPD or other monomers are shown in the second row of Fig. 1 [7,9].

☆ This paper has been submitted as a contribution to a Thematic Issue on Mechanism of Molecular Catalysts edited by Kuiling Ding and Matthias Beller.

* Corresponding authors at: Biological and Chemical Research Centre, Faculty of Chemistry, University of Warsaw, Żwirki i Wigury Street 101, 02-089 Warsaw, Poland, MS also at: Laboratory of Electrochemistry, Faculty of Chemistry, University of Warsaw, Pasteur 1, 02-093 Warsaw, Poland.

E-mail addresses: mskomps@chem.uw.edu.pl (M. Skompska), prof.grela@gmail.com, akajetanowicz@cnbc.uw.edu.pl (K. Grela).

[1] Current address: Apeiron Synthesis S.A., Duńska 9, 54-427 Wrocław, Poland.

https://doi.org/10.1016/j.jcat.2018.05.014
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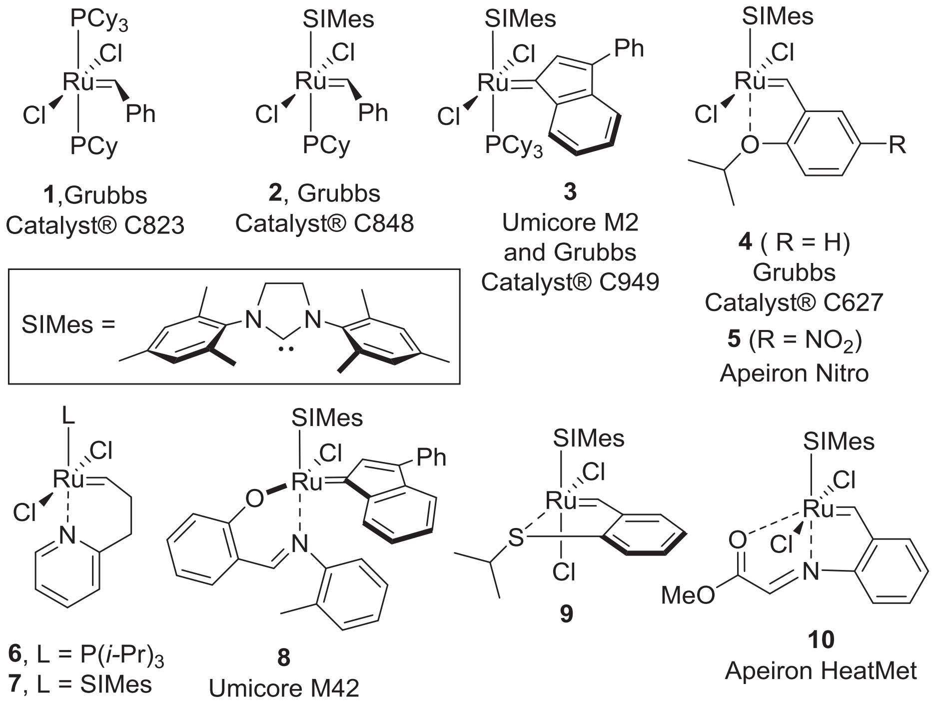
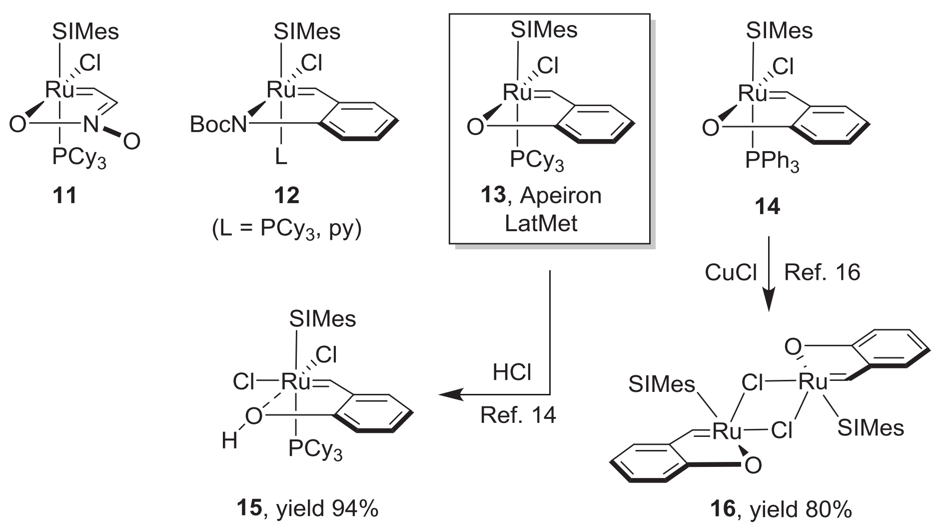


Fig. 1. Selected general (**1**–**5**) and latent (**6**–**10**) olefin metathesis catalysts (Cy = cyclohexane).



Scheme 1. Ru-azinate (**11**), amide (**12**) and phenolate (**13**–**14**) complexes (py = pyridine).

Recently, we have communicated on chelating latent ruthenium-azinate salt (**11**) [10], Ru-amide (**12**) [11], and Ru-phenolate (**13**) [12] complexes that exhibit high latency, but can be activated by heat or acidic additives (Scheme 1) [13]. In particular, catalyst **13** was found to be very useful in ROMP of DCPD because of excellent thermo-stability and high solubility in a neat monomer compositions. As a result, this catalyst meet some interest from industry and was eventually commercialized under a trade name of LatMet [9c].

Importantly, the same Ru-phenolate complex has been independently and in the same time studied by Pietraszuk et al. [14]. The authors elucidated the mechanism of precatalyst **13** activation with HCl by an elegant combination of spectroscopic (^{1}H and ^{13}P NMR, FTIR) and computational methods, to conclude that it involves the formation of catalytically active hydroxybenzylidene complex **15**, which was eventually isolated in a good yield (Scheme 1). Interestingly, also copper salts, a well-known phosphine scavenger [15], was found to activate **13** (although in less extent than HCl) [14]. In a follow-up paper by Pietraszuk et al., similar studies were extended to another LatMet analogues, and in the case of triphenylphosphine bearing analogue **14** the product of reaction with CuCl was isolated and fully characterised (**16**, Scheme 1) [16].

Finding an effective non-acidic chemical polymerisation triggers is of practical value, as HCl and other strong Brønsted acids can lead to problems, such as polymerisation equipment corrosion or acid-catalysed side reactions of a monomer. Previously, we noted that metathesis reactions of some latent Ru alkylidene complexes proceed faster in presence of CCl_4 used as a solvent or an additive [10]. Looking for non-acidic activators of Ru-phenolate