



Editor's choice paper

Non covalent immobilization of pyrene-tagged ruthenium complexes onto graphene surfaces for recycling in olefin metathesis reactions



Houssein Nasrallah^a, Stéphane Germain^b, Pierre Queval^b, Caroline Bouvier^a, Marc Mauduit^b, Christophe Crévisy^{b,*}, Emmanuelle Schulz^{a,*}

^a Institut de Chimie Moléculaire et des Matériaux d'Orsay, CNRS UMR 8182, Université Paris-Sud, Université Paris-Saclay, bâtiment 420, 91405, Orsay cedex, France

^b Ecole Nationale Supérieure de Chimie de Rennes, CNRS UMR 6226, 11 allée de Beaulieu, CS 50837, 35708, Rennes cedex 7, France

ARTICLE INFO

Article history:

Received 1 September 2016

Received in revised form

30 September 2016

Accepted 4 October 2016

Available online 5 October 2016

Keywords:

Metathesis

Ruthenium

Reduced graphene oxide

Immobilization

Catalyst reuse

ABSTRACT

Synthesis of Hoveyda-type ruthenium complexes, modified by pyrene tags on the NHC ligand and/or the benzylidene moiety, is described. Thanks to non-covalent π - π interactions these new complexes were immobilized on carbon supports [reduced graphene oxide (rGO) or graphene] and their activity and recoverability for metathesis reactions have been studied. A SIPr-based complex possessing the pyrene function on the benzylidene ligand (**C2**) delivered the best results for the ring closing metathesis of diethyldiallyl malonate as benchmark reaction. The presence of additional pyrene-functionalized styrenyl-ether as ligand to the rGO-supported catalyst (**C2/L@rGO**) noticeably improved the recycling procedure allowing supplementary efficient catalytic runs. This may be due either to a facilitated boomerang effect or to a gradual release of the active species in solution. Finally, catalyst **C2/L@rGO** was proven to be successfully used to promote metathesis reactions in a multisubstrate procedure, the same supported-catalyst batch being successively engaged to transform three different substrates, in diene and ene-yne RCM reactions.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Olefin metathesis is undeniably a key reaction for fine organic synthesis [1] and the specific use of ruthenium-based complexes allowed transformations to be selectively run at the very end preparation of complex molecular architectures [2]. Nevertheless, use of such metallic complexes induces high costs and furthermore may lead to some ruthenium leaching in the reaction media, which must be necessarily avoided at least for pharmaceutical applications [3]. In such a context, the search for a compromise is still relevant for the use of highly active catalysts which in turn may reveal low stability. Numerous research teams are thus making significant efforts to develop such species aiming at increasing the turn over number [4]; on the other hand, various studies are ongoing to fine tune recycling methods for efficient homogeneous supported catalysis [5].

Two different procedures have been studied for grafting the catalytic species on a support, either via a covalent functionalization

[6] or thanks to non-covalent interactions [7]. Immobilization of the catalyst through reversible interactions is often more favorable because less demanding in tedious chemical transformations. Furthermore, support recovery may also be envisaged, for instance, after catalyst deactivation. Such strategies have already been described for immobilization of various catalysts through ionic linkage [8], hydrogen bonding [9] and we also described formation of charge transfer interactions in such a context [10]. Quite recently, use of graphitic surfaces [11] has also been reported for immobilizing homogeneous complexes mainly through strong π , π -interactions between the support and pyrene-tagged ligands. Such carbon materials are rather inert and stable species and they generally possess quite large surface areas. For instance carbon nanotubes (CNT) have already been described as efficient support to immobilize and recover homogeneous catalysts via non-covalent interactions. This strategy has already been used to perform asymmetric catalysis; Zhou and his group modified thus enantiomerically pure PypPhos ligand by a covalent pyrene link and carried out the rhodium-catalysed heterogeneous asymmetric hydrogenation of α -dehydroamino esters [12]. Some of us prepared pyrene-tagged bis(oxazoline) copper complexes and proved the efficient reactivity of such complexes immobilized on carbon supports (charcoal, fullerene, single-walled CNT) in promoting

* Corresponding authors.

E-mail addresses: christophe.crevisy@ensc-rennes.fr (C. Crévisy), emmanuelle.schulz@u-psud.fr (E. Schulz).

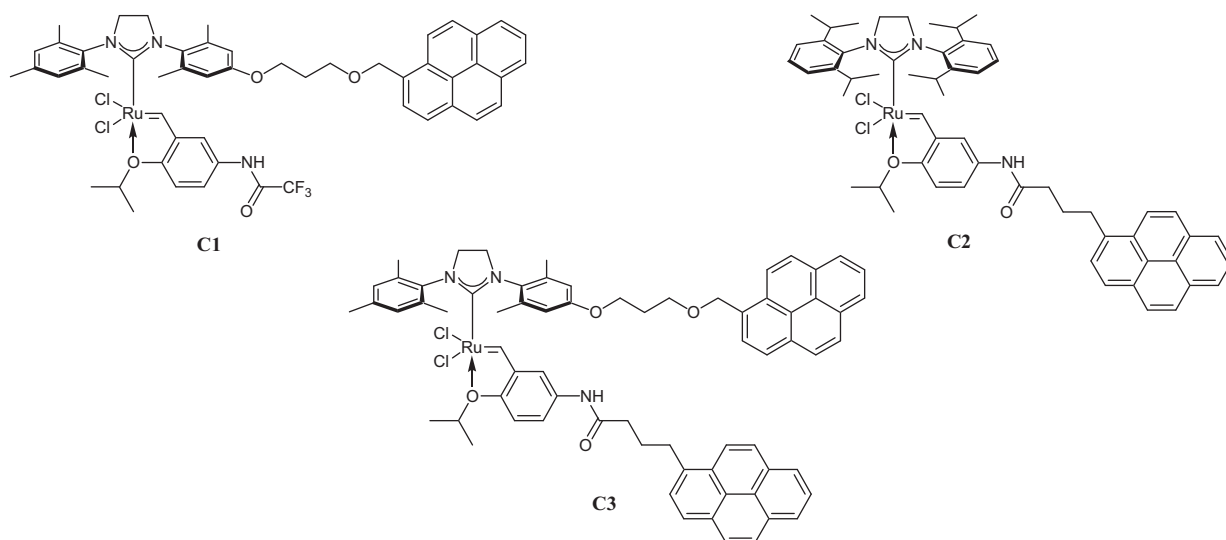


Fig. 1. Pyrene-tagged Ru complexes **C1**, **C2** and **C3**.

Henry and ene reactions under recycling conditions [13]. A similar strategy was developed by Riant and Hermans to immobilize and recycle gold complexes on CNT for enyne cyclisation [14]. Wang and his group also synthesized a pyrene-tagged ruthenium complex and, in the presence of single-walled CNT, they achieved stable and recyclable catalytic species to promote ring-closing metathesis reactions, as the only example of this type of interactions involved for such transformations [15]. Other related supports have been used in this context and particularly carbon-coated magnetic nanoparticles which afford not only catalysts support but also easy handling and recovery by magnetic decantation [16]. Thus pyrene-tagged dendritic palladium catalysts immobilized via π -stacking on such nanoparticles allowed efficient Suzuki couplings [17]. The group of Mata and Peris [18] interestingly used chemically derived graphenes such as reduced graphene oxide (rGO) for immobilizing pyrene-modified palladium and ruthenium complexes active in various reactions, including a co-immobilization for hydrodefluorination. It is in this context that the present study was set, aiming at immobilizing ruthenium catalysts for recycling experiments in metathesis reactions through ligand modifications by pyrene moieties either at the carbene or benzylidene ligand.

2. Results and discussion

2.1. Catalysts preparation

A tag dedicated to immobilization can be introduced on a Hoveyda type Ru complex either on the NHC ligand [5,10] or on the benzylidene one [5,15]. As it can be expected that the location of the tag may have a critical influence on the behavior of the resulting pre-catalysts, both options were considered in this study. We decided to synthesize complex **C1** (Fig. 1) which bears the pyrene group on the NHC ancillary ligand and also a trifluoroacetamido group on the benzylidene ligand. The SIPr-based complex **C2** (Fig. 1), where the pyrene tag is linked to the benzylidene ligand via an amide bond was also synthesized. As the benzylidene ligand is liberated during the pre-catalyst activation phase, good reusability properties would necessarily arise in this case either from a boomerang mechanism or a reservoir effect [19]. Finally, the influence of the presence of two pyrene tags, held by both ligands was also tested (complex **C3**, Fig. 1). Moreover, as the presence of a trifluoroacetamido group (found only in **C1**) or a SiPr (found only in **C2**) are known to exert some influence on both the activation

phase and the stability of the pre-catalysts [20], differences in the reactivity of these three species were expected.

Complexes **C1** and **C3** were obtained from tagged Ru complex **7** (Scheme 1), which was stemmed from imidazolium salt **6** and complex **M1**[®] RuCl₂(PCy₃)₂(Ind) following a standard procedure already employed for the synthesis of similar anthracene-tagged complexes [10]. Imidazolium salt **6** was obtained following the convergent strategy depicted in Scheme 1. 1-Pyrene methanol was linked to 4-bromo-2,5-dimethylphenol through two successive nucleophilic displacements from 1-bromo-3-chloropropane to afford compound **2** in a good overall yield. Besides, crude amide **3** was formed by a two steps procedure consisting in a coupling of 2,4,6-trimethylaniline and *N*-Boc-Glycine followed by a removal of the carbamate protecting group. LiAlH₄ mediated reduction of the amide group led to the crude diamine **4** in quantitative overall yield over 3 steps. Diamine **4** was isolated in a nearly pure form and was engaged in the next step without any further purification. Then, aryl bromide **2** and amine **4** were coupled using a Buchwald-Hartwig reaction [21], to give pyrene-tagged bis-aniline **5** in good isolated yield after purification (81%). The latter was converted to the tetrafluoroborate imidazolium salt **6** following a standard procedure. Pure NHC precursor **6** was isolated in a good yield (80%) after precipitation in a CH₂Cl₂/AcOEt mixture. Imidazolium salt **6** was first treated with potassium *tert*-amylate, thus reacted 1 h at 80 °C with Ru complex **M1**[®] to afford the pyrene-tagged Ru indenylidene complex **7** in high yield (86%) after silica gel chromatography.

The synthesis of Hoveyda-type pyrene-tagged complexes **C1**, **C2** and **C3** was next undertaken. *N*-(4-Isopropoxy-3-vinylphenyl)-4-(pyren-1-yl)butanamide **8** (Scheme 2) had to be produced in order to achieve the synthesis of **C2** and **C3**, which have a pyrene tag on the benzylidene-ether ligand. Pyrene-tagged compound **8** was obtained in good yield (74%) by a DCC/DMAP mediated coupling between 4-(pyren-1-yl)butanoic acid and known [22] 4-isopropoxy-3-vinylaniline hydrochloride.

The Ru complex **7** was converted to **M7**₁[®]-type complex **C1** by treatment with 2,2,2-trifluoro-*N*-(4-isopropoxy-3-vinylphenyl)acetamide [23] and CuCl. The latter was isolated in high yield (90%) after silica gel chromatography followed by a precipitation in a CH₂Cl₂/pentane mixture. The syntheses of complex **C2** and bis-tagged complex **C3** were achieved by reaction of pyrene-tagged styrenyl compound **8** with respectively (SIPr)RuCl₂(PPh₃)(Indenylidene) **M23**[®] and tagged Ru complex **7**.

Download English Version:

<https://daneshyari.com/en/article/4757857>

Download Persian Version:

<https://daneshyari.com/article/4757857>

[Daneshyari.com](https://daneshyari.com)