



Account/Revue

Organometallic catalysis: From concepts to selected applications[☆]Mathieu Sauthier^{a,b}, Philippe Zinck^{a,b}, André Mortreux^{a,b,*}^a Université Lille Nord-de-France, 59000 Lille, France^b Unité de catalyse et chimie du solide (UMR8181 CNRS) ENSCL, université Lille-1, sciences et technologies, BP 90108, 59652 Villeneuve d'Ascq cedex, France

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ABSTRACT

This article is devoted to the use of some concepts of organometallic chemistry for their application in homogeneous catalysis developed in our laboratory in Lille and presented in the Gecom-Concoord meeting in Albé. The first examples will deal with the use of bifunctional ligands, where it will be shown that designing an aminophosphine ligand allows one to improve the rate of linear dimerization of dienic substrates by two orders of magnitude, as compared with the same reaction conducted in protic media. Another application will concern the use of the hemilability character of a suitable methoxy substituted, sterically hindered alkoxy ligand, responsible for the original metathesis reaction of terminal acetylenes. The second part will be devoted to the use of transmetalation reactions, at first in polymerization reactions, where the concept of Coordinative Catalyzed Chain Growth Transfer will be established using Lanthanide complexes and magnesium dialkyls, applied to olefins, conjugated dienes, styrene and isoprene/styrene statistical copolymerization. The last topic will develop carbonylation reactions using boronic acids and enones or alkynes, in which the key step is a transmetalation/carbonylation sequence, opening the way to new catalytic carbonylation processes.

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R É S U M É

Cet article de revue décrit quelques réactions originales mises au point au laboratoire de Lille et présentées lors du Gecom Concoord à Albé en juin 2009, et dont la particularité est d'avoir été mises en place en exploitant quelques concepts de base de chimie organométallique. Le premier exemple décrit a trait à l'utilisation de ligands bifonctionnels, par lesquels il est montré que le design d'un ligand aminophosphinite permet d'augmenter la vitesse de la réaction de dimérisation de diènes conjugués de deux ordres de grandeurs comparativement à la même réaction effectuée en milieu protique. Une autre application concerne l'utilisation du concept d'hémilabilité d'un ligand stériquement encombré de type alkoxy éther, permettant de réaliser de manière originale la métathèse sélective d'alcynes vrais. La seconde partie sera consacrée à l'exploitation de la notion de transmétallation, où le concept de catalyse de croissance de chaîne par coordination et transfert entre un catalyseur lanthanidocène et les dialkylmagnésiens a été mis en évidence sur l'éthylène, puis étendu par un choix judicieux des ligands aux α -oléfines, au butadiène, à l'isoprène, au styrène et finalement à la copolymérisation

Mots clés :

Catalyse

Couplage CC

Métathèse

Transmétallation

Transfert

Polymérisation

Carbonylation

[☆] Dedicated to the memory of John Osborn, on the occasion of this meeting organized thanks to the organizing committee from Strasbourg University, where he spread his brilliant and clever knowledge of organometallic chemistry and catalysis.

* Corresponding author.

E-mail address: andre.mortreux@ensc-lille.fr (A. Mortreux).

statistique isoprène/styrène. La dernière partie développée dans cet article implique l'utilisation du monoxyde de carbone dans des réactions de formation de liaison CC à partir d'acides boroniques et d'énones ou alcynes. L'insertion de CO par formation attendue de liaison métal acyle subséquente à la transmétallation ouvre une voie nouvelle à la synthèse de dérivés carbonylés.

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1. Introduction

The basic principles of organometallic chemistry are the basis of the discovery of catalysts and catalytic processes involving CC bond formation or rearrangement, such as olefin and diene polymerizations, olefin and alkyne metathesis, as well as carbonylation reactions.

In this review, we will focus essentially on four typical reactions, which have been the subject of investigations in our lab, aimed at both the improvement of known catalytic processes as well as the establishment of new catalytic reactions.

Namely, this article will deal first with the use of the hemilability concept in catalysis and coordination chemistry, for which reviews have appeared in the literature [1,2]. Two reactions will be described: the linear diene dimerization and codimerization on nickel based catalysts modified by bifunctional ligands and the discovery of an alkoxyether-tungsten based dinuclear complex for its use as precursor for terminal alkyne metathesis.

The second part will focus on transmetalation reactions applied to catalysis. We will first emphasize the role of ligands on lanthanides to produce catalysts used in polymerization, and describe a coordinative chain growth reaction that allows the synthesis of well defined higher Grignard reagents from magnesium dialkyls used in excess via a reversible, transmetalation reaction between the chain growing on lanthanide and magnesium. Applied first to ethylene and α -olefins in our lab, this process will be shown to be generalized to styrene and dienes. The last part will be devoted to rhodium catalyzed carbonylation reaction, by which it will be demonstrated that under suitable conditions, Suzuki-Miyaura type reaction using boronic acids and enones or terminal alkyne may be conducted under CO. As a result, CO insertion into the rhodium-aryl bond formed via transmetalation is occurring, allowing carbon monoxide to be inserted in the following step of the catalytic cycle and produce new carbonylated compounds.

2. Hemilability and catalysis: Carbon–Carbon coupling using aminophosphinite–nickel catalysts

2.1. Linear dimerization of conjugated dienes

Linear dimerization of butadiene has been developed in the mid-1960s on nickel carbonyl–phosphine-based catalysts in the presence of alcohols [3] and revisited by Heimbach in the early 1970s, using nickel-based catalysts modified by phosphite ligands in the presence of morpholine [4]. In the same way, Pittman and Smith showed that upon reducing $\text{NiBr}_2(\text{PPh}_3)_2$ with NaBH_4 , linear dimers

are also produced in the presence of ethanol [5]. As compared with the use the same catalytic systems in non protonic, apolar solvents such as toluene, where the reaction course is well known to produce cyclic rather than linear dimers [5] (Fig. 1), we have been interested in the synthesis of a suitable bifunctional, phosphorus ligand which would provide a phosphonite moiety to coordinate nickel, and bearing a pendant NH moiety which would act as the proton donor, playing the same role as morpholine and ethanol in the selective production of linear dimers.

To achieve this goal, we started from a chemistry we were developing related to the synthesis of new chiral ligands for asymmetric catalysis, namely that of the so-called AminoPhosphinePhosphinite (AMPP) ligands from aminoalcohols [5], during which synthesis a monophosphinylation could selectively lead in one step to an aminophosphinite ligand bearing a NH moiety on the β carbon atom vs the phosphinite. Such a reaction is depicted in Scheme 1, using ephedrine as the starting aminoalcohol, leading to the new EPHOSNH ligand 1.

As shown in Table 1, the reactivity of this system in toluene, where 1 equivalent of the hemilabile EPHOSNH is used as bifunctional ligand for nickel based catalyst

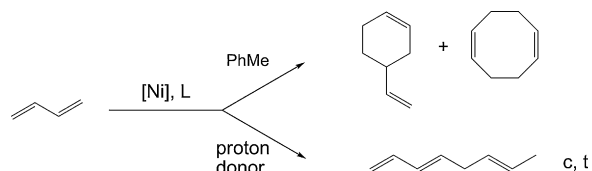
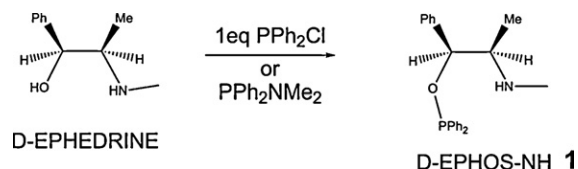


Fig. 1. Cyclic vs linear dimerization of butadiene.



Scheme 1. Monophosphinylation of ephedrine: synthesis of the EPHOSNH aminophosphinite ligand.

Table 1

Linear dimerization of butadiene into 1,3,6 –octatrienes: comparative results.

| Catalyst | Butadiene/ Ni | Conv. (mol%) | Rtion time (T °C) |
|--|------------------|-----------------|----------------------|
| $\text{Ni}(\text{COD})_2/\text{EPHOS-NH}$ (1/1) | 600 | 90 | 15 min, 60 °C |
| $\text{Cl}_2\text{Ni}(\text{PPh}_3)_2/\text{NaBH}_4/\text{EtOH}$ | 600 | 80 | 24 h, 80 °C |
| $\text{Ni}^0/\text{P}(\text{OEt})_3/\text{Morpholine}$ | 800 | 50 | 24 h, 60 °C |

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