C. R. Chimie 16 (2013) 343–349

Contents lists available at SciVerse ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com

Account/Revue

New research areas inspired by sustainable development

Éric Da Silva [a], Wissam Dayoub [a], Nicolas Duguet [a], Estelle Métay [a], Florence Popowycz [b], Marc Lemaire [a,*]

[a] Laboratoire de catalyse, synthèse et environnement, institut de chimie et de biochimie moléculaires et supramoléculaires, ICBMS-CNRS-UMR 5246, université Claude-Bernard–Lyon-1, bâtiment Curien, 43, boulevard du 11-Novembre-1918, 69622 Villeurbanne cedex, France

[b] Laboratoire de chimie organique et bio-organique, institut national des sciences appliquées (INSA-Lyon), ICBMS-CNRS-UMR 5246, bâtiment Jules-Verne, 1er étage, 20, avenue Albert-Einstein, 69621 Villeurbanne cedex, France

ARTICLE INFO

Article history:
Received 18 October 2012
Accepted after revision 20 December 2012
Available online 23 January 2013

Keywords:
Green chemistry
Polyhydrosiloxanes
Glycerol
$ScCO_2$
C(sp^2)–H activation

ABSTRACT

More than 20 years after its birth, green chemistry has definitely entered its golden age. In this account, we highlight some of our progress made over the last 10 years towards the development of green methodologies. We investigated various aspects of green chemistry such as new reagents, catalysts, transformations and solvents and also the utilization of renewable resources. We report herein four mature projects illustrating our efforts in these fields: (1) polyhydrosiloxanes as new reducing agents; (2) glycerol as a new platform for amphiphilic molecules; (3) water, room-temperature ionic liquids and supercritical carbon dioxide as new solvents and (4) C(sp^2)–H activation as new C–C bond formation methodology. An overview of each project is given and the potential applications are discussed.

1. Introduction

Waste minimization has always been a consideration since the beginning of industrial chemistry. As early as the 19th century, Ernest Solvay depicted a clean process for the production of sodium carbonate that generates only water and calcium chloride as ultimate by-products, thus ending the polluting “Leblanc process”. If this discovery had been made today, it would have been surely called green chemistry. Since the term has been coined by Paul Anastas in 1991 and the 12 principles have been erected as guidelines for its development, this concept has emerged as a new field on its own, having now its own scientific community, peer-reviewed journals, specialized meetings and so on. The main reason for this fast-growing interest is not only the awareness of sustainable development but also the fact that it provides new challenges for both academic and industrial researchers. One striking example is the preparation of 2,5-furandicarboxylic acid (2,5-FDCA) from renewable resources. This product has recently drawn a lot of attention for the potential replacement of phthalates in polymers such as polyesters or polyamides. The production of FDCA is in the focus of many chemical industries but is also of great interest from a fundamental point of view; new, cleaner and safer methodologies should be developed in order to render its access as green as possible.

In our laboratory, green methodologies have been developed for several years, keeping in mind that they should be amenable to large scale and easily transferable to industry. That is why, in most of the cases, our projects were conducted in collaboration with industrial partners. These partnerships led us to explore many different aspects of green chemistry, such as the development of new, cleaner and safer reagents, catalysts, transformations and solvents and the utilization of renewable resources as feedstock. Herein, we illustrate each facet with a mature project:

- new reduction methodologies using polyhydrosiloxanes for the replacement of boron and aluminum hydrides;

---

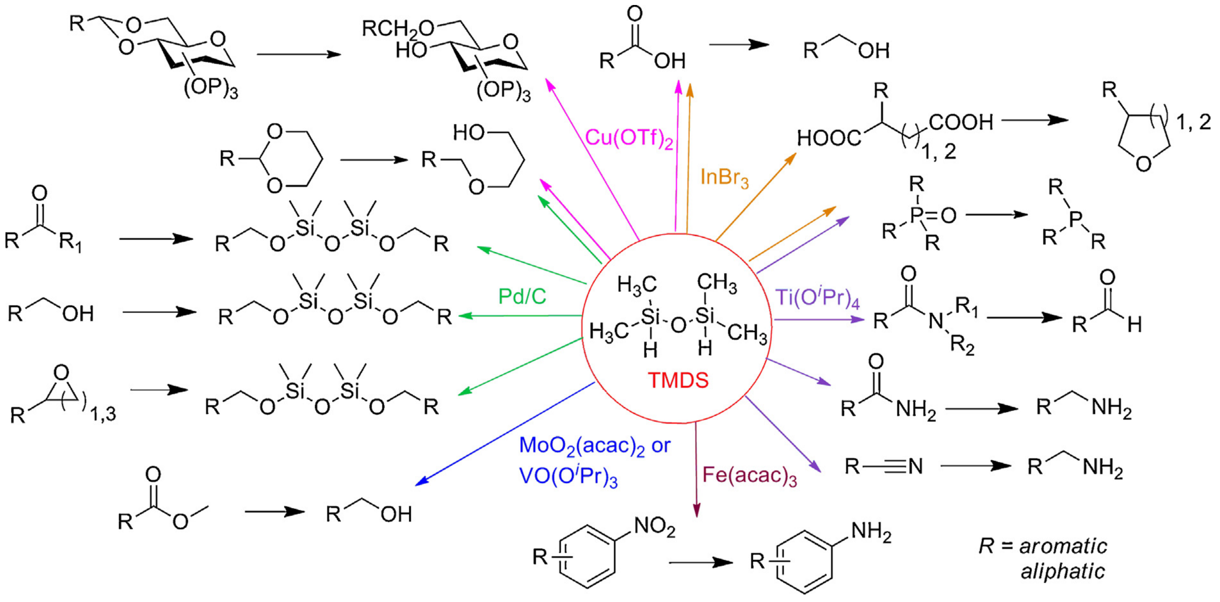
* Corresponding author.
E-mail address: marc.lemaire.chimie@univ-lyon1.fr (M. Lemaire).

1631-0748/$ – see front matter © 2013 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.
http://dx.doi.org/10.1016/j.crci.2012.12.019

- valorization of glycerol through reductive alkylation with aldehydes or acids;
- use of water, ionic liquids or supercritical carbon dioxide as low-environmental impact solvents;
- C(sp^2)–H activation methodologies as alternatives to classic cross-coupling reactions.

2. New reagents: reduction with tetramethyl-disiloxane for the substitution of classic hydrides

Nowadays, it is necessary to design and elaborate new processes and reagents in order to reduce or eliminate the safety risks (both for operators and production chains) linked to the utilization of hazardous substances. The reduction of different functions (amide, ketone, aldehyde or ester) can be performed with high selectivity and efficiency with boron and aluminum hydrides. These reducers, produced at 2000–3000 t/year and widely used in industry, are dangerous partly due to their extreme reactivity with water [1]. They are often used in excess and reactions are usually performed in water-soluble solvents [2]. Treatment of such reactions is often complex due to the large production of salts which are potentially toxic [3–5] and present in large quantities. An alternative to these technologies is the development of silicon hydrides associated with organometallic complexes [6]. Indeed, the ultimate waste of silicon derivatives is inert. Among silicon hydrides, hydrosilanes have been known to selectively reduce organic functions depending on the nature of the associated metal. However, even if the results are highly interesting in term of efficiency and selectivity, there remain some risks to exploit these compounds notably due to their toxicity and their flammability. Moreover, some of them ($HSi(OEt)_3$ or $HSiCl_3$), in the presence of a transition metal, can generate, via a redistribution reaction, a highly pyrophoric gas (SiH_4). These drawbacks can explain the limitation to the development of these methodologies in large scale [7]. On the other side, polyhydrosiloxanes, which are relatively cheap and stable (in air and water), can also be used for the reduction of organic functions even in industry. Polymethyl-hydrosiloxane (PMHS) is typically a colourless liquid that is soluble in most organic solvents and inert towards air and moisture [8]. PMHS, which is prepared from cyclic siloxanes, is commercially available and has shown promising results for the reduction of organic functions, in some cases with good enantio-selectivity. Amongst polyhydrosiloxanes, tetramethyl-disiloxane (TMDS) offers several benefits in comparison with PMHS. Notably the formation of a gel during the reaction was never observed with TMDS and the quantity of hydride is usually close to the stoichiometry. TMDS is issued from silicon industry and the by-product obtained at the end of the reaction can be employed as a water-repellent treatment of materials. Nevertheless, until now, it was less explored [9–11]. With the collaboration of two industrial partners, we have previously reported the utilization of TMDS for the reduction of a large variety of organic functions. The initial study was dedicated to the reduction of phosphine oxides (Scheme 1). The reduction of secondary and tertiary phosphine oxides has been performed in the presence of TMDS and $Ti(O^iPr)_4$. Mechanistic studies have shown the formation of a Ti^{III}/Ti^{IV} cluster which could be the active species [12]. The same metallic complex with TMDS can efficiently reduce nitriles to amines and amides to aldehydes [13]. The replacement of titanium derivative by an iron complex allows the reduction of aromatic nitro to the corresponding aniline [14]. Using palladium on charcoal, alkoxy-silanes can be prepared from alcohols, aldehydes or ketones and via the ring-opening of cyclic ethers [15]. By working in acidic medium with the same palladium complex, acetals give alcohols in high yields [16]. Copper triflate associated with TMDS can reduce both acetals and carboxylic acids



Scheme 1. TMDS as a nucleophilic hydride source for the reduction of organic functions.