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A computational view on the reactions of hydrocarbons with coinage metal complexes

Maria Besora ^a, Atualpa A.C. Braga ^b, W.M.C. Sameera ^c, Juan Urbano ^d,
Manuel R. Fructos ^d, Pedro J. Pérez ^d, Feliu Maseras ^{a, e, *}

^a Institute of Chemical Research of Catalonia (ICIQ), Avda. Països Catalans 16, 43007 Tarragona, Catalonia, Spain

^b Departamento de Química Fundamental, Instituto de Química Universidade de São Paulo, Av. Prof. Lineu Prestes, 748, Bl. 05 sup. Sl. 0552 Butantã, São Paulo, SP, Brazil

^c Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto 606-8103, Japan

^d Laboratorio de Catálisis Homogénea, Unidad Asociada al CSIC,

CIQSO-Centro de Investigación en Química Sostenible and Departamento de Química y Ciencia de Materiales, Universidad de Huelva, 21007 Huelva, Spain

^e Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Catalonia, Spain

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ABSTRACT

Computational chemistry plays a key role in the construction of the current understanding of the reaction mechanisms for the reaction of coinage metal complexes with hydrocarbons. Carbene precursors (diazo compounds) or nitrene precursors (hypervalent iodine compounds or azides) react with the catalyst complexes giving rise to highly reactive metalcarbene or metallonitrene intermediates, which are difficult to observe experimentally. DFT calculations allow the characterization of these intermediates and of their reactivity with hydrocarbons, leading to C–H insertion, aziridination or oxazole synthesis. This review summarizes computational work in the last decade in this research field, which has progressed in collaboration with experimental knowledge on these systems.

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Introduction

Hydrocarbons are cheap and abundant materials. They are not only used as energy sources (mostly as fossil fuels), but also play a substantial role as feedstock in chemical industry. The latter application is however hindered by the stability of the compounds, which make them difficult to functionalize. This functionalization is vital, because it enables the conversion of cheap and abundant substrates into valuable functionalized organic compounds [1–3].

Several strategies have been used to functionalize unreactive hydrocarbons through metal mediated processes. A key group among these processes is the metal-assisted C–H bond activation, which participates in a number of catalytic cycles, and has been

discussed in previous excellent reviews [4–6]. Among the most common mechanisms for C–H activation, we can find well-known processes such as oxidative addition/reductive elimination, sigma bond metathesis or electrophilic activation. In all these cases, the activation process introduces the hydrocarbon in the inner-sphere coordination of a metal. Then, a new metal–substrate bond is formed, and C–H bond activation occurs.

Interestingly, other approaches can be used for the functionalization, such as the use of coinage-metal based catalysts with the tris(pyrazolyl)borate or N-heterocyclic carbene based ligands. Among the best known of these alternative methods, we can find the C–H bond functionalization by carbene insertion or the unsaturated hydrocarbon functionalization by nitrene addition. These processes are different from the conventional transition metal complex catalysed C–H/C–C bond activation processes in the sense that there is no hydrocarbon coordination to the metal centre. In fact the avoidance of the formation of the new M–C and/or M–H bonds is one of the advantages of these mechanisms (see below).

* Corresponding author. Institute of Chemical Research of Catalonia (ICIQ), Avda. Països Catalans 16, 43007 Tarragona, Catalonia, Spain. Tel.: +34977920202; fax: +34977920231.

E-mail addresses: fmaseras@icq.es, feliu.maseras@uab.cat (F. Maseras).

C–H bond functionalization of hydrocarbons by carbene insertion can be achieved by using the reaction of a diazo-compound with a metal catalyst. The diazo-compound and the metal complex generate *in situ* a transient metalcarbene intermediate and nitrogen gas. Then, metalcarbene ($[M] = CR_1R_2$) can be inserted into a hydrocarbon (R–H), forming the functionalized product (R–CR₁R₂H), see [Scheme 1](#) (top).

Functionalization of hydrocarbons is also possible *via* nitrene addition to unsaturated C=C bonds, see [Scheme 1](#) (bottom). A metallonitrene intermediate is formed *in situ* from iminoiodanones and chloramine-T. A similar, yet quite different, reaction can take place with the addition of a similar metallonitrene (formed in this case from an azide) to a C≡C bond. The resulting substrate in this case is not a 3-membered ring with a double bond, but an expanded ring is formed with other atoms of the substrate (*i.e.*, a 5-membered ring, see below).

This review is focused on the mechanistic computational studies of the coinage metal-based alternative methods of hydrocarbon functionalization. Excellent reviews have summarized the research performed in the area, mainly focussing on the experimental work [5,7–9]. Computational chemistry is very helpful for the mechanistic understanding of these processes because of the difficulty of isolating the highly reactive intermediates from the experimental studies.

Methodology

In this work we summarize different computational studies carried out during the last decade. During this time, the computational approaches have evolved, some methods have improved, and new tools have appeared. As a result of this, the studies we summarize in this article include a variety of methodologies. The main conclusions of each work hold despite eventual inadequacies of the particular methods, but care must be taken when comparing numerical results. The earlier work focused mainly on potential energies in gas phase. The improvements in methods, software and hardware, allow nowadays to compute free energies of species optimized in solution. In between the two approaches, there are a large number of studies in which the effect of the solvent was not taken into account for the optimization, but performing single point calculations on the gas phase optimised structures. The choice of the density functional has also been changed over the years. Initial studies were performed by using the popular B3LYP method [10–13], and later studies applied with the meta-hybrid M06 functional [14]. More recently, dispersion effects (missing in B3LYP and only partially incorporated in M06) have become

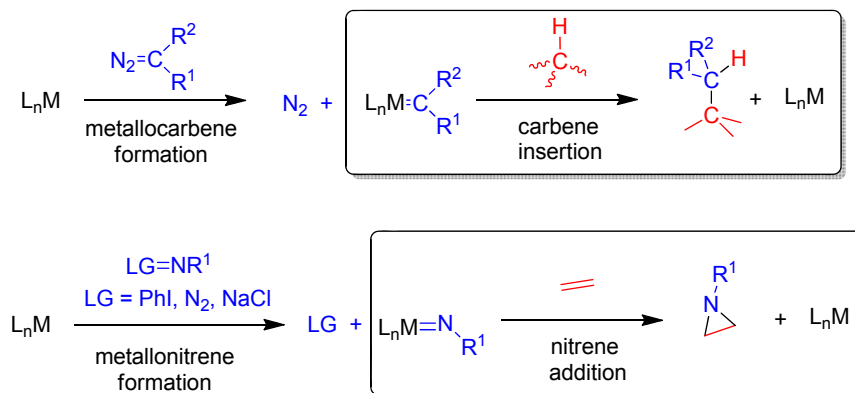
popular, and commonly applied under one of Grimme's approaches (DFT-D [15], DFT-D2 [16], or DFT-D3 [17] or B97D). In some cases, the dispersion corrections were included as a single point calculation, while in others they were also taken into account during the optimization. The basis sets used have not been changed much during these years, although recent advances of the hardware allows us to extend the use of polarization functions for almost all atoms of the system. The basis sets for the transition metals and associated effective core potentials (ECPs) have moved from the previous very popular LANL2DZ [18,19] to the currently most popular SDD [20,21].

Metal-promoted carbene insertion into saturated hydrocarbons

The reaction

Functionalization of C–H bonds with carbene sources is a quite recent and powerful tool. Pérez [5,9,22,23], Dias and Lovely [24–26], Doyle [7] and Davies [8] research groups have devoted significant contributions for the development of this chemistry. In this approach, the diazo compounds and hydrocarbons react with a metal catalyst to form a functionalized substrate, see [Scheme 1](#). In fact, the diazo compound reacts with the catalyst to extrude the nitrogen molecule, forming a metalcarbene. The metalcarbene is then inserted in an intermolecular fashion to the C–H bond of the corresponding alkane. The functionalized substrate is formed and the metal catalyst is recovered. This reaction has been successfully applied with catalysts of coinage metals (Cu, Ag, Au) and Rh with a variety of alkanes (linear and branched). C–H functionalization with rhodium catalysts has been mainly studied in the group of Doyle and Zhou, and it has been extensively reviewed elsewhere [7]. It is interesting to highlight a computational study on the insertion of carbenes into C–H bonds with a dirhodium tetracarboxylate catalyst was reported by Nakamura et al. [27], obtaining a mechanism through metalcarbene intermediates similar to the one that will be described in the next sections. Musaev's group also carried out an interesting computational study, suggesting that a bis(imino)pyridine chloro iron complex could effectively catalyze the C–H bond functionalization [28], but this has not been experimentally confirmed.

There is a consensus in the chemical community that the C–H functionalization process takes place through a metalcarbene intermediate. The possibility of having the metal playing a pure Lewis acid role inducing the formation of a free carbene was proposed. However, it is no longer accepted [29–32].



Scheme 1. Schematic representation of the C–H bond functionalization by carbene insertion (top) and nitrene addition into C=C bonds (bottom).

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