

Preface

The homogeneous platinum- and gold-catalyzed transformation of unsaturated precursors is a very active area in the field of catalysis research. Indeed information about new novel reactions and modified, improved, metal complexes is published every week. These findings involve interesting and sometimes surprising changes in the molecular connectivity, which can often be applied to a growing number of applications in total synthesis.

The rapid expansion of this field is due to the peculiar Lewis acid properties of the concerned metals. The alkynophilic character of these soft metals and the π -acid carbophilic activation of unsaturated groups promote the intra- or intermolecular attack of nucleophiles to form carbon-carbon and carbon-heteroatom bonds.

The pioneering efforts in this area in the early 1990s utilized simple metal salts, such as halides because of their apparent insensitivity under aqueous conditions and ability to successfully promote a diversity of synthetic transformations. But a decade later, Au(I) cationic species have proven to be superb catalysts. The chemistry of π -complexes of gold finally underwent an explosive growth when novel complexes were used successfully as catalysts for a rapidly growing number of important reactions or transformations of alkynes, alkenes and allenes.

These catalysts allow us to overcome additional problems associated with other metal complexes that also promote the same transformations, such as Hg salts, since they are considered essentially nontoxic. Furthermore, they combine high affinity to the π system with the advantages of a kinetically labile carbon-metal bond that can be readily cleaved under the reaction conditions. These reactions provide an atom-economical entry into functionalized cyclic and acyclic scaffolds useful for the synthesis of natural and non-natural products under mild conditions with excellent chemoselectivity and high synthetic efficiency.

Although this protocol gives rise to a wide range of transformations and shows a large versatility, an array of mechanistic hypotheses has been formulated to account for the results, leading many times to a diversity of mechanistic proposals for the same reaction. Therefore, a mechanistic interpretation is needed to direct and improve a given process. The theoretical underpinnings have been considered recently and, despite computational analyses being less abundant, they have become a useful

tool for rationalizing the role of the molecular structure of precursor and catalyst and accounting for the versatility of these reactions.

In this book, we provide a perspective on the mechanisms as suggested by theoretical calculations and discuss the most significant physical features and results obtained in this fascinating research area. In particular, the description of the probable intermediates, given their transient nature, has provided critical information about the reaction pathways.

The layout of this book is as follows. Chapter 1 presents an overview of the theoretical properties of the reactant complexes and of the nature of the likely key reaction intermediates. It is focused on the results reported on the structure, bonding and reactivity. A correlation of the catalytic behavior with the available structural data, coordination chemistry, and reactivity patterns, including relativistic effects, is provided which allows the underlying principles of catalytic carbophilic activation by π -acids to be formulated.

In Chapter 2 a review of the recent and seminal advances in 1,*n*-enynes cycloisomerization reactions in the presence of carbophilic transition metals is described. These compounds have emerged as highly useful and important precursors for this synthetic protocol. The recent mechanistic insights, the enantioselective versions and the applications in total synthesis are highlighted.

Chapter 3 analyzes the rearrangement of propargylic esters, a block of essential and versatile precursors. The description of different mechanisms taken from the recent literature in which stereoselectivity, with special focus on chirality transfer and memory of chirality phenomena, is shown. The chapter starts with reactions involving simpler rearrangements and adds steps until more complex reaction cascades with highly functionalized substrates.

Chapter 4 focuses on N-heterocyclic carbenes (NHC), a family of complexes as effective alternatives to classical tertiary phosphines as catalysts in transition metal catalyzed transformations. The rapid development of this area is a result of synergic interactions between experimental and computational chemists. The authors detail how computer modeling has proven extremely useful to rationalize the experimental data and to accelerate the pace at which this chemistry is being developed.

Chapter 5 provides an insight into the activation of allenes and allenynes by gold complexes toward nucleophilic attack. It is focused on the various possible geometries of allene-gold species. While some retain the stereochemical information of the starting optically active allenes, others may lose it by planarization. To shed light on this, the factors governing axial-to-center chirality transfer are described. Some concepts are illustrated by selected examples of transformations analyzed computationally.

Chapter 6 shows how computational studies can be a useful complementary tool to experimental methodology. In this case, the elucidation of mechanisms and regioselectivity of heterocyclization of allenes catalyzed by late transition metals.

Finally, the theoretical analyses of the reaction mechanisms for gold-catalyzed cycloaddition reactions involving allenes and dienes have been assessed in the Chapter 7. This family of reactions gives different products, six- and seven-membered rings depending on the nature of the catalyst. According to the published

theoretical studies, the mechanisms proposed for the [4C+3C] and [4C+2C] intramolecular cycloadditions are detailed.

We have tried to cover the most relevant computational studies on the main topics in this research area, from the physical properties of the noble-metal catalysts to the most important transformations catalyzed by them. In some cases this has required more detailed theoretical chapters. Other topics have focused more on the practical application of computational chemistry as a valuable and complementary tool to the experimental research.

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