Iridaaromatics via Methoxy(alkenyl)carbeneiridium Complexes

Subjects: Chemistry, Inorganic & Nuclear

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The development of a versatile methodology to synthesize polycyclic metallaaromatic hydrocarbons based on iridium, as well as the studies that helped to determine and understand what is required in order to broaden the scope and the selectivity of the methodology and stabilize the complexes obtained. This methodology aims to open the door to new materials based on graphene fragments.

metallaaromatics iridium PAHs PMAHs

1. Introduction

The interest of graphene lies in its structure and unusual physical properties, which turn polycyclic aromatic hydrocarbons (PAHs) and nanographenes, small graphene fragments, into the subject of several research in the last decades [1]. Studying PAHs allows for correlating their geometrical and electronic structure with their properties, which can then be applied to larger structures. It has been found that the introduction of defects or irregularities in the structure of PAHs modifies their properties and consequently broadens their field of application. Among these defects, the most common are deviations from planarity due to edges, the introduction of non-six-member rings, doping with heteroatoms or the inclusion of substituents for their functionalization [2][3][4][5].

The introduction of these irregularities in PAHs can lead to new materials improving results and even opening up new applications with respect to their non-defective analogues. With this in mind, over the last decade our research group has focused its interest on the development of new PAHs by incorporating a transition metal in order to create polycyclic metallaaromatic hydrocarbons (PMAHs) by replacing a CH unit with a transition metal. These new systems are considered to be doped PAHs and could potentially introduce a slight deviation of the plane. This has led us to develop a synthetic and versatile methodology that allows us to obtain PMAHs with different structures and sizes, as this is the key to obtaining new and improved properties for their application in the field of materials.

In this review, we focus on the studies which led us to the successful development and understanding of a methodology for synthesizing iridium based PMAHs.

2. Current Insights

In recent years our versatile synthetic methodology has allowed us to obtain different topologies of metallaaromatic complexes, such as iridanaphthalenes, iridaphenanthrenes, iridanthracene, rhodafurans or the spirobifluorene iridanaphtalene.

The key of our methodology is the precursor, a methoxy(alkenyl)carbene complex, which by C–H bond activation of one of the *ortho* carbons of an aromatic substituent on *γ* carbon leads to the formation of a metallaaromatic compound. In order to guarantee the success of this methodology, we have studied the influence of different substituents at the γ carbon, the metallic center, the substituents on the aromatic cycle and the possibility of using it to obtain different topologies. Therefore, it was concluded: 1) the necessity of one of the substituents on the *γ* carbon to possess a large steric hindrance in order to obtain a single *Z* or *E* isomer; 2) the existence of a second substituent, also aromatic, ensures the formation of the metallaaromatic complex due to its capability of delocalize the electronic density among the whole complex; 3) and, in this case, at least one of them not be substituted in the *ortho* positions; 4) the increase of aromatic rings increases stability; 5) the most favored *ortho* position for C–H bond activation is the one that gives the less stressed cycle; and 6) the capacity of the methodology to synthesize different topologies is very broad.

All together gives the opportunity to synthesize analogues to polycyclic aromatic hydrocarbons, PMAHs, which are small fragments of graphene doped with a transition metal and thus to study their new properties and consequently their applications in the field of materials.

References

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