HABILITATION THESIS
-ABSTRACT-

Contributions to the Chemistry of Group 14 Elements

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This thesis contains a synthesis of my scientific activity, showing the advances made especially in the field of low coordinate heavy *p*-block elements, as well as presenting the current projects and the main perspectives that are envisaged. My scientific activity is focused on the chemistry of element-organic compounds of *p*-block elements, particularly in the chemistry of unsaturated species containing heavy elements of group 14 and 15, and their use for obtaining various coordinative compounds.

The first research direction consists of the preparation and characterization of unsaturated species involving E=C=P or E-C=P moieties (E = Si, Ge, Sn, P, As, Sb). These types of compounds, named heterophosphaalkenes and –allenes, appear interesting from both academic and applicative points of view. This research brings new knowledge on fundamental aspects, such as structural parameters, the nature of the chemical bonds, the formation and stabilization of the unsaturated E=C system, the effect of the substituents linked to the heavy atoms of the molecular skeleton etc. The reactivity study of these compounds is also interesting, due to the existence of multiple reaction sites, such as the multiple double bonds, the lone pairs of electrons of the hetero-elements, the vacant orbitals, etc. The research carried out in this direction has been focused on finding the most efficient methods of stabilizing this kind of derivatives. Thus, several unsaturated systems containing silicon, germanium and tin atoms in an E-C=P or E=C=P moiety have been studied. It should be emphasized that the first stable phoshastannapropenes were obtained and characterized in our research group. Once these compounds are stabilized, due to their multiple reaction sites, they are promising as building blocks in organometallic chemistry, as precursors of new materials with controlled properties

and as ligands. On the other hand, coordinative compounds containing heterophosphaalkenyl units as ligands can present catalytic or biologic activity. To modulate the compounds' properties and thus their applications, it is important to find the corresponding stabilization methods. For this, the most common techniques employed include the use of different bulky substituents and/or coordination to transition metals. This latter method, that provides both steric and electronic stabilization effect, is frequently used in our group.

More recently, I have been involved in a second direction of research, focusing on another topic, the chemistry of low-valent organometallic compounds, specifically the heavy analogues of carbenes, known as metallylenes. In this case, two methods of stabilization were closely studied: metallylenes containing a phosphaalkenyl moiety and a carbene unit in their structure or intramolecular coordination using sulfur based pincer-type ligands. Some significant results regarding the synthesis and coordination ability towards transition metals of the metallylenes containing -P=C< units were obtained which were reported in several articles in highly rated journals. For example, we have reported a new bis(phosphaalkenyl)germylene and -stannylene of NHC–E(II)[C(Cl)=PMes*]$_2$ (E = Ge, Sn, Mes* = 2,4,6-tri-*tert*-butylphenyl; NHC=[:C{N(*i*Pr)C(Me)$_2$}]) type, the first representatives of a new class of metallylenes, using both the phosphaalkenyl –P=C< unit as ligand and the stabilizing coordination properties of the NHC (N-heterocyclic carbenes). In the second case, where the synthesis of metallylenes could be achieved through intramolecular stabilization using monoanionic aryl pincer type ligands, new germylenes and stannylenes were obtained with new bis-sulfone and sulfone-sulfoxide pincer-type ligands and their behavior towards transition metal carbonyls was evaluated. The results obtained so far in this topic are very promising and were published in high impact journals.

Considering the significance of the advances made in the field of heavy analogues of carbenes, it is appropriate to continue this research, primarily in order to establish the influence of both steric and electronic effects on the stabilization of these types of low-valent derivatives. Moreover, this can bring new knowledge about

the chemistry of these compounds and lead to potential applications (as catalysts or biological activity).

This work contains the results obtained in the two main research topics that were studied. Furthermore, some secondary research directions, that I have recently approached, will also be briefly presented.

The second part entitled “Scientific perspectives” contains the main research topics, presented briefly, that I propose to address in the following period.

The references were inserted in the text, as footnotes, as close as possible to the place where they were cited.