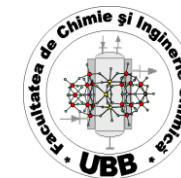




# Synthesis and characterization of *p* and *d* element containing complexes using chelating type ligands

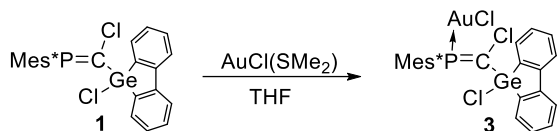
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## Introduction

The synthesis of new complexes containing both *p* and *d* block elements is a topic of interest because of the possibility to explore the synergic effect of such structures on their stability and applications. For this, the first step is the design and synthesis of the adequate ligand system. Our research group studied different *p*-block element containing compounds and their role as ligands for transition metal complexes.<sup>1</sup> Among these, unsaturated compounds incorporating  $-P=C-E<$  moieties ( $E =$  heavier group 14 group atom), are of interest, because of their enhanced reactivity and particular features. Lately a new compound class was designed and obtained, containing a  $>P=C-Ge$  moiety, where the germanium atom is included in a fluorenyl cycle.<sup>2</sup> (Compounds **1** and **2**, Scheme 1 and 2)



Mes\* = 2,4,6-tri-tert-butylphenyl

Scheme 1. Reaction of phosphalkenyl germanium ligand **1** with  $AuCl(SMe_2)$ .

Reactions of ligand **2** with either bis(acetonitrile)dichloropalladium(II) or dichloro(1,5-cyclooctadiene)palladium(II) (Scheme 2) led to the formation of the new complex **5**, evidenced by  $^{31}P$  NMR spectroscopy, showing a singlet signal resonance at 236.3 ppm, upfield shifted compared to the starting bis(9-chloro-9-phosphaalkenylchloro)-9-germafluorene **2**. Complex **5** was fully characterized by NMR spectroscopy and single crystal X-ray diffraction.<sup>3</sup> (Figure 2) In the case of the reaction of ligand **2** with  $AuCl(SMe_2)$  (Scheme 2) the formation of complex **4** was seen, suggested by the upfield shift of the signal observed in the  $^{31}P$  NMR spectra at 238.4 ppm, from 290.1 ppm for ligand **2**. Complex **4** was characterized by multinuclear NMR spectroscopy. Attempts to obtain single crystals suitable for X-ray analysis were not successful. Their structural features of complexes **3-5** were also assessed by means of theoretical calculations.

The coordination ability of 9-chloro-9-phosphaalkenylchloro-9-germafluorene (**1**) and bis(9-chloro-9-phosphaalkenylchloro)-9-germafluorene (**2**) was evaluated towards different transition metal complexes in order to evaluate their role to act as ligands. At first complexes with gold(I) and palladium(II) fragments were obtained and successfully characterized through multinuclear NMR spectroscopy and single crystal X-ray diffraction.<sup>3</sup> Gold complex **3** was fully characterized by multinuclear NMR spectroscopy and single crystal X-ray diffraction.<sup>3</sup> (Figure 1)

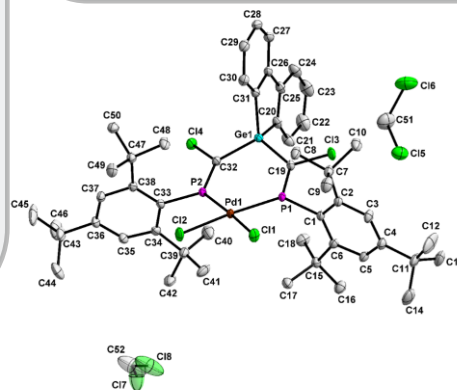


Figure 2. Asymmetric unit in the crystal of **5**, shown with 50% probability ellipsoids (hydrogen atoms are omitted for clarity).

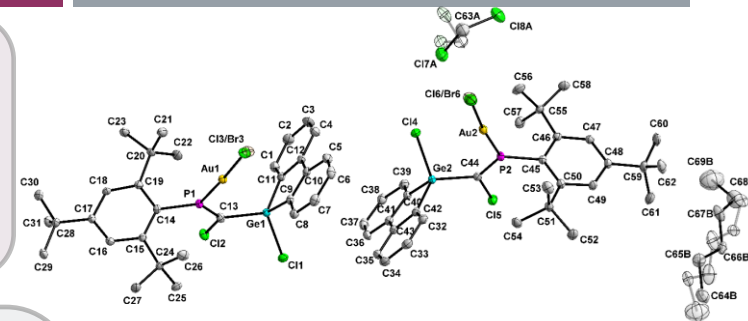
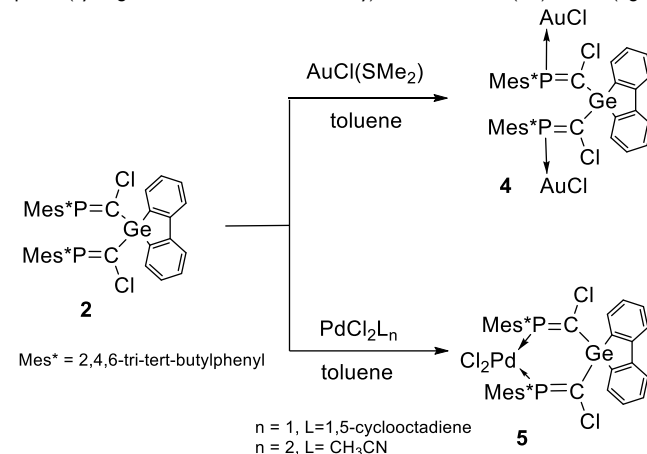


Figure 1. The asymmetric unit of **3**  $CH_2Cl_2 \cdot n-C_6H_{14}$ , shown with 50% probability ellipsoids (hydrogen atoms are omitted for clarity) with isomers **3a** (left) and **3b** (right).



Scheme 2. Reaction of diphosphaalkenyl germanium ligand **2** with palladium and gold precursors.

## Conclusions

New complexes **3-5** were obtained through the coordination of the phosphalkenyl germanium ligands **1** and **2** towards gold and palladium precursors, show good stability in inert atmosphere, and were fully characterized in solution and in solid-state. Owing to their enhanced stability given by the particular structure of the ligands (**1** and **2**) and due to the presence in the same molecule of a metalloid (i.e. germanium) and a transition metal, such *p-d* complexes might display interesting catalytic properties. Our further plans include the testing of the complexes for their catalytic activity.

## Acknowledgment

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## References

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