# Pincer típusú ligandumokat tartalmazó vegyületek vizsgálata számításos kémiai módszerekkel

# Investigation of pincer ligand-based compounds using computational methods

**DEAK Noémi, ATTIA Amr, NEMEȘ Gabriela**

Babeș-Bolyai University, Faculty of Chemistry and Chemical Engineering,

Arany János street, no.11, 400028, Cluj-Napoca, Romania, noemi.deak@ubbcluj.ro

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## Introduction

Sulphur containing compounds, particularly those having sulfinyl and sulfonyl moieties, have a wide range of applications.[1] They can be used for example in organic and organometallic synthesis, as ligands in catalyst structures, as fine chemicals and pharmaceuticals, or in biologically relevant compounds. [1] Furthermore, sulfone-based compounds have been shown to contribute to the stabilization of p- and d-block elements by having the role of donor groups in chelating type ligands. [2]

## Aim of the study

In the present work, we investigated the synergistic effects resulting from the combination of the previously studied sulfinyl and sulfonyl moieties with various phosphine and phosphonate functional groups. For this purpose, a series of molecules were evaluated in order to elucidate the electronic and steric effects associated with the two distinct functional groups using computational methods. Density functional theory (DFT) calculations and molecular modeling were employed to assess the coordination potential of these compounds as novel ligands, with particular emphasis on their ability to stabilize p- and d-block derivatives for potential applications in catalysis.

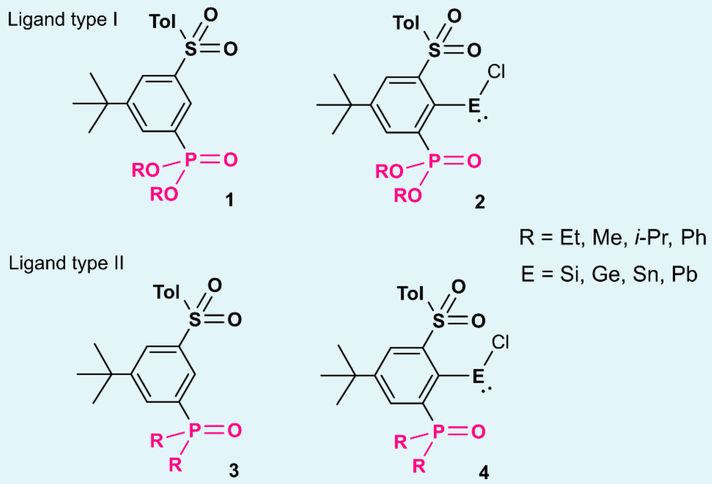



Figure 1. General structure of sulfone-phosphonate ligands and their stabilized tetrylenes characterized by DFT studies.

## Results and discussions

The geometry of the target structures were fully optimized using density functional theory (DFT) with the hybrid PBE0 functional paired with the def2-TZVP triple-ζ valence basis set. The case for the germanium containing tetrylene is exemplified in Figure 2, denoted as structure 2, with R = Et variant.

The optimized structure features a tridentate pincer ligand coordinating germanium via the central aryl *ipso*-carbon and oxygen atoms from phosphonate and sulfonate arms, with an additional chloride ligand, resulting in a four-coordinate germanium center (Figure 2). To explore ligand tuning, analogous structures with different substituents on phosphorus ($Me_2$, $iPr_2$, $Ph_2$) were optimized at the same level of theory. Key bond distances are compared in Table 1.

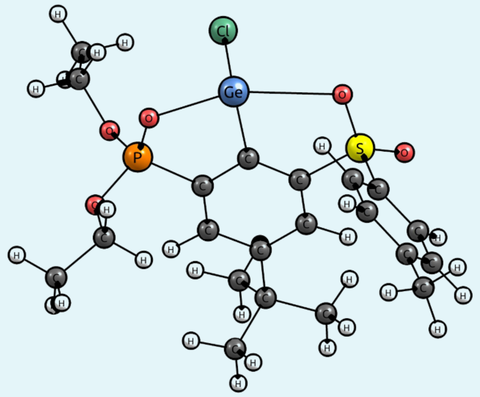



Figure 2. Optimized geometry in the case of the germylene 2 with R = Et.

Table 1. Comparison of bond distances across variants for germylenes 2 (Å)

| Bond / R | Et | Me | *i*-Pr | Ph |
|---|---|---|---|---|
| Ge–C | 2.073 | 2.073 | 2.071 | 2.072 |
| Ge–O(P) | 2.138 | 2.148 | 2.129 | **2.058** |
| Ge–O(S) | 2.65 | 2.636 | 2.648 | **2.517** |
| Ge–Cl | 2.263 | 2.259 | 2.259 | 2.249 |

The optimized geometry reveals a distorted tetrahedral coordination environment around germanium. The notably elongated Ge–O(S) distance (~2.65 Å) indicates weaker coordination from the sulfonyl oxygen compared to the phosphonate, consistent with an asymmetric pincer binding mode. The Ge–C and Ge–Cl bonds fall in typical ranges for organogermanium species, but overall metrics suggest significant distortion from ideal tetrahedral geometry due to the constraints of the pincer ligand.

The frontier molecular orbitals (HOMO and LUMO, Figure 3) were analyzed in detail for the studied tetrylenes. Visualization of the frontier orbitals provides complementary insight into reactivity and electronic structure (isosurface plots at the same computational level).

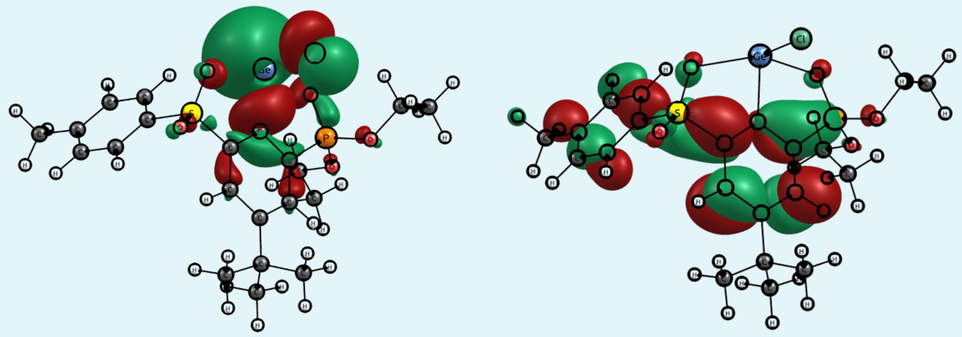


Figure 3. HOMO and LUMO orbitals of germylene 2.

## Conclusions

This work demonstrates that the novel sulfone-phosphonate is well-suited as a ligand platform for stabilizing low-valent group 14 elements. Computational analyses reveal a unique electronic profile, identifying the resulting tetrylenes as promising candidates for catalysis.

References

[1] I. Fernández, N. Khiar, Chem. Rev. 103, 3651–3706 (2003). [2] N. Deak, D. Madec, G. Nemes, Eur. J. Inorg. Chem., 2769-2790 (2020).
[3] N. Deak, O. Thillaye du Boullay, S. Mallet-Ladeira, I.-T. Moraru, D. Madec, G. Nemes, Eur. J. Inorg. Chem, 3729-3737 (2020).

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