

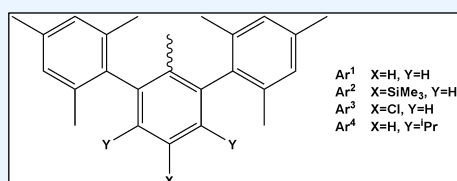
Introduction

The outstanding success of terphenyl-based ligands in low coordination main group and transition metal chemistry¹ and spectacular findings in this field inspired the calculation and synthesis of tetrylenes stabilized by terphenyl-systems with varying remote substituents on the backbone of the central aromatic ring. These modifications can dramatically influence chemical properties and bonding in main group and transition metal complexes.²

Calculations on the series of modified terphenyl-based systems included geometry optimization and simulation of ¹H- and ¹³C-NMR-spectra. The same compounds were synthesized and characterized by a range of spectroscopic methods (multinuclear NMR, UV-Vis, X-ray-diffraction).³

Calculations and Synthesis

To compare the spectroscopic properties and structural aspects influenced by the ligand modification on the backbone of the terphenyl-based system Ar¹EAr² (E=Ge,Sn) a series of ligands Ar²-Ar⁴ was calculated and synthesized in addition to previously reported Ar¹.

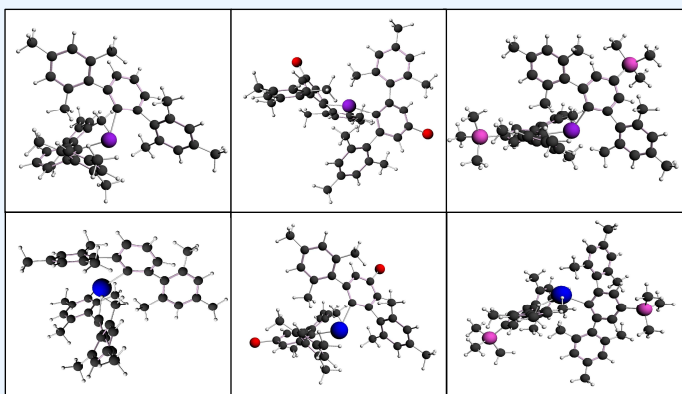


Scheme 1: Modification of terphenyl ligands

Structure optimization was performed using mPBE with the TZ2P basis set as implemented in ADF (Version 2007.01).

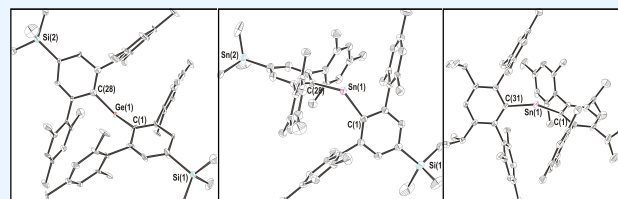
Compound	C-E-distance 1 [Å]	C-E-distance 2 [Å]	C-E-C-angle [deg]
Ar ¹ GeAr ¹	2.217	2.304	119.7
Ar ² GeAr ²	2.193	2.482	130.4
Ar ³ GeAr ³	2.168	2.465	131.9
Ar ¹ SnAr ¹	2.524	2.398	121.7
Ar ² SnAr ²	2.406	2.486	124.2
Ar ³ SnAr ³	2.459	2.411	120.3

Table 1: Calculated geometries of the modified terphenyl ligands



Scheme 2: Optimized structures of the modified terphenyl ligands

Synthesis of the same range of terphenyl ligands provided access to experimental structure data obtained by X-ray-diffraction.

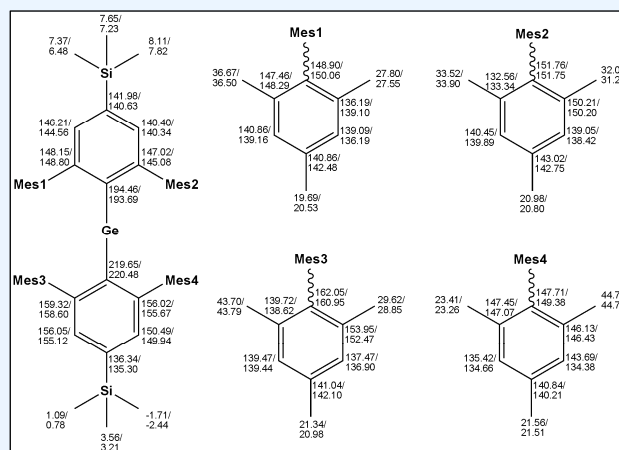


Scheme 3: X-ray-crystal structure of Ar²GeAr², Ar²SnAr² and Ar⁴SnAr⁴

Compound	C-E-distance 1 [Å]	C-E-C-angle [deg]
Ar ¹ GeAr ¹	2.033(7)	114.4(4)
Ar ² GeAr ²	2.017(5)	115.11(3)
Ar ¹ SnAr ¹	2.225(5)	114.7(2)
Ar ² SnAr ²	2.241(3)	115.61(27)
Ar ⁴ SnAr ⁴	2.258(2)	123.10(17)

Table 2: Experimental geometries of the modified terphenyl ligands

Simulation of NMR-spectra was performed on the b3lyp/6-311+G** and b3lyp/cc-pVTZ level as implemented in Gaussian 03. Theoretical data showed the same trends as observed by experimental methods.



Scheme 4: ¹³C-NMR shifts [ppm] for Ar²GeAr² in the order 6-311+G**/cc-pVTZ
 Experimental shifts: -1.72, 20.66, 21.46, 128.77, 134.30, 136.49, 136.55, 139.56, 141.46, 143.97, 170.33 ppm.

Conclusion and Outlook

A range of sterically encumbering ligand systems have been investigated by DFT calculations as well as by synthesis and experimental methods. Analogous trends could be observed concerning geometry parameters as well as NMR shifts.

UV-VIS-spectra will be simulated in order to compare the results with already obtained experimental data. In further work plumblylenes will be also considered in order to complete the series of heavier tetrylenes.

References

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- 2 R.C. Fischer, L. Pu, J.C. Fettingner, M. Brynda, P.P. Power, *J. Am. Chem. Soc.*, **2006**, *128*, 11336.
- 3 P.M. Wilfling, M. Flock, R.C. Fischer, *unpublished results*.