

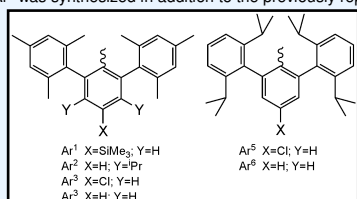
Introduction

The outstanding success of terphenyl-based ligands in low coordination main group and transition metal chemistry¹ and spectacular findings in this field inspired the synthesis of di- and trifunctional sterically encumbering building blocks.² Remote substituents on the back bone of the terphenyl ligands can dramatically influence chemical properties and bonding in main group and transition metal complexes.³

The successful synthesis of a range of di- and trifunctional ligands provided access to polynuclear, divalent group 14 complexes and extended systems. A series of divalent group 14 element derivatives was synthesized and investigated by spectroscopic methods (¹³C-, ¹¹⁹Sn- and ²⁰⁷Pb- NMR, UV-VIS, X-ray).

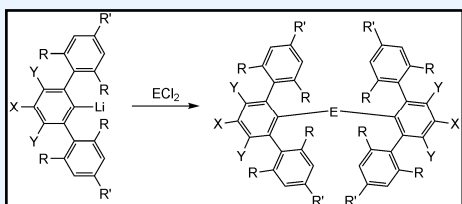
Synthesis and Reactions

To test the effect of electronically modified ligands on structural aspects and spectroscopic properties on terphenyl based tetrylenes ArⁿEAⁿ (E=Ge, Sn, Pb) a series of ligands Ar¹-Ar³, Ar⁵ was synthesized in addition to the previously reported Ar⁴ and Ar⁶.



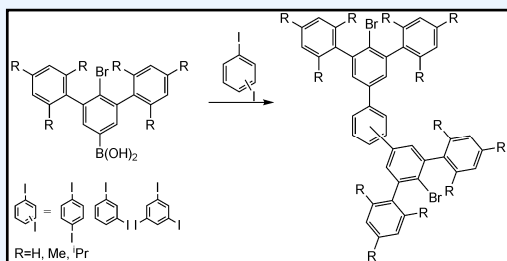
Scheme 1 Modified terphenyl ligands

Reaction of the lithio derivatives with heavier group 14 dichlorides ECl₂ (E=Ge, Sn, Pb) afforded the corresponding tetrylenes in good yields



Scheme 2 Synthesis of heavier tetrylenes

Starting from di- and triido benzene and terphenyl based boronic acid Ar⁷, di- and trinuclear ligands were obtained following routes given in scheme 3.



Scheme 3 Synthesis of di- and trinuclear terphenyl ligands

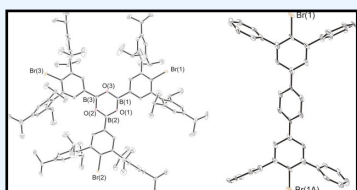


Figure 1 X-ray crystal structures of trimeric Ar⁷ and Ar⁸
 (Pr groups omitted for clarity or Ar₉)

In contrast to Dipp (2,6-Pr₂-C₆H₃) substituted derivatives, where electronic trends are obscured by steric effects of the flanking aryl groups, the mesityl (2,4,6-Me₃-C₆H₃) substituted derivatives clearly follow trends in NMR shifts and UV-VIS absorption maxima with respect to electron withdrawing or releasing substituent pattern.

Compound	UV-VIS-max. (nm)	δ ipso- ¹³ C (C-E) (ppm)	δ ¹¹⁹ Sn (ppm)	δ ²⁰⁷ Pb (ppm)
Ar ¹ GeAr ¹	583	170.4		
Ar ² GeAr ²	622	173.1		
Ar ³ GeAr ³	565	168.0		
Ar ⁴ GeAr ⁴	578	169.6		
Ar ¹ SnAr ¹	555	193.2	1975	
Ar ² SnAr ²	591	199.7	2077	
Ar ³ SnAr ³	535	188.5	1891	
Ar ⁴ SnAr ⁴	553	192.0	1971	
Ar ⁵ SnAr ⁵	600		2151	
Ar ⁶ SnAr ⁶	600		2235	
1,4-Ar ¹ SnAr ² SnAr ⁴	606		2061	
1,4-Ar ⁵ SnAr ⁶ SnAr ⁵	555		1932	
Ar ¹ PbAr ¹	528	307.1		8778
Ar ² PbAr ²	570	328.9		9593
Ar ³ PbAr ³	513	300.4		8609
Ar ⁴ PbAr ⁴	526	305.2		8844
Ar ⁵ PbAr ⁵	572			10287
Ar ⁶ PbAr ⁶	586			9430

Table 1: UV-VIS-maxima and ¹³C-, ¹¹⁹Sn- and ²⁰⁷Pb NMR shifts

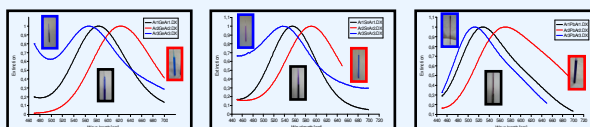


Figure 2 UV-VIS-spectra of ArⁿEAⁿ, Ar²EA² and Ar³EA³, E=Ge, Sn, Pb

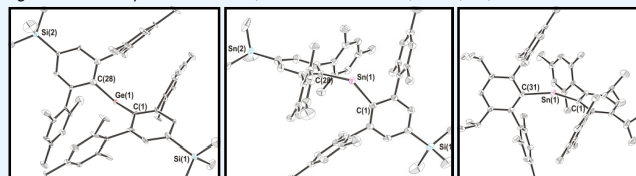


Figure 3: X-ray-crystal structures of Ar¹GeAr¹, Ar¹SnAr¹, Ar²SnAr²

Compound	C-E-distance [Å]	C-E-C-angle [deg]
Ar ¹ GeAr ¹	2.017(5)	115.11(3)
Ar ⁴ GeAr ⁴	2.037(7)	114.4(4)
Ar ¹ SnAr ¹	2.241(3)	115.61(27)
Ar ² SnAr ²	2.258(2)	123.10(17)
Ar ⁴ SnAr ⁴	2.225(5)	114.7(2)
Ar ⁵ SnAr ⁵	2.197(4)	118.73(7)
Ar ⁶ SnAr ⁶	2.225(2)	117.56(8)
Ar ⁴ SnAr ⁴	2.334(12)	114.5(6)
Ar ⁵ SnAr ⁵	2.356(5)	118.70(15)
Ar ⁶ PbAr ⁶	2.390(8)	121.5(3)

Table 2: Crystallographic data of various ArⁿEAⁿ-compounds

Conclusion and Outlook

A range of sterically encumbering ligand systems have been synthesized and characterized by various spectroscopic methods like multinuclear NMR, UV-VIS and X-ray-diffraction. Additionally the results were compared to DFT-based calculations of the products.

A significant change of these characteristics could be observed and correlated with the different remote substituents at the back bone of the ligands. Further research on this topic will include the extension to larger ligand systems and further characterisation of the products.

References

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- 3 R.C. Fischer, L. Pu, J.C. Fettinger, M. Brynda, P.P. Power, *J. Am. Chem. Soc.*, **2006**, 128, 11336.
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