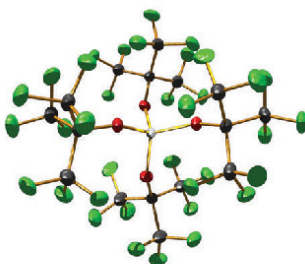




Marcin Gonsior (Autor)
**From Cationic Silver Complexes to Reactive
Phosphenium- and Arsenium-Intermediates
Stabilized by Weakly Coordinating Anions**

Marcin Gonsior

**From Cationic Silver Complexes to Reactive
Phosphenium- and Arsenium-Intermediates
Stabilized by Weakly Coordinating Anions**



Cuvillier Verlag Göttingen

<https://cuvillier.de/de/shop/publications/2476>

Copyright:

Cuvillier Verlag, Inhaberin Annette Jentzsch-Cuvillier, Nonnenstieg 8, 37075 Göttingen,
Germany

Telefon: +49 (0)551 54724-0, E-Mail: info@cuvillier.de, Website: <https://cuvillier.de>

Table of Contents

Chapter A. Introduction to Chemistry with Weakly Coordinating Anions	1
A.1 Definition of the Term “Weakly Coordinating Anion” (WCA)	1
A.2 Applications of Weakly Coordinating Anions in Fundamental and Applied Science	2
A.3 An Overview to Known Types of WCAs	6
A.4 Fluorinated Alkoxyaluminates $[\text{Al}(\text{OR}^{\text{F}})_4]^-$: A Series of WCAs Extended by Our Group	11
A.5 Weakly Coordinating Anions - Theoretical Background	13
A.6 Aim of This Work	17
A.7 References to Chapter A	24
Chapter B. A $[\text{F}_2\text{Al}(\text{OR}'')_3]_2^-$ Dianion Coated by Three Thallium Cations in the $[\text{Tl}_3\text{F}_2\text{Al}(\text{OR}'')_3]^+[\text{Al}(\text{OR}'')_4]^-$ Salt $\{\text{R}'' = \text{C}(\text{H})(\text{CF}_3)_2\}$	33
B.1 Introduction to the Chemistry of Aluminum-Fluorine Compounds	33
B.2 Preparation of Tl^+ Salts of WCAs	34
B.3 Discussion of the Formation of B1	43
B.4 Conclusion to Chapter B	46
B.5 Experimental Procedures to Chapter B	47
B.7 References to Chapter B	48
Chapter C. Synthesis and Characterization of a Fluoride Bridged Anion $[(\text{RO})_3\text{Al}-\text{F}-\text{Al}(\text{OR})_3]^-$ $\{\text{R} = \text{C}(\text{CF}_3)_3\}$	51
C.1 Introduction	51
C.2 Synthesis of a Silver Salt of the $[(\text{RO})_3\text{Al}-\text{F}-\text{Al}(\text{OR})_3]^-$ Anion and its Spectroscopic Properties	53
C.3 Investigations on Formation and Stability of the New WCA	62
C.4 Conclusion and Outlook to Chapter C	65
C.5 Experimental Procedures to Chapter C	65
Chapter D. Silver Complexes of Cyclic Hexachlorophosphazene	71
D.1 Complexes of Cyclic Phosphazenes $(\text{PNY}_2)_n$ ($n = 3$)	71
D.2 Preparation and Characterization of the $\text{Ag}^+(\text{P}_3\text{N}_3\text{Cl}_6)$ Complexes	72
D.3 SIA, Energetics and Bonding of the $\text{Ag}^+(\text{P}_3\text{N}_3\text{Cl}_6)$ Complexes	86
D.4 Conclusion and Outlook to Chapter D	92

D.5 Experimental Procedures to Chapter D	93
D.6 References to Chapter D	96
Chapter E. Cationic P-S-X Cage Compounds (X = Br, I)	99
E.1 On Neutral and Ionic Phosphorus Sulfides	99
E.2 Insertion Reactions of a Carbenoid "PX ₂ ⁺ " (X = Br, I)	100
E.3 Synthesis and Characterization of the Products of the "PX ₂ ⁺ " Insertion Reaction into the P ₄ S ₃ Cage	101
E.4 Investigations of the Metastable [P ₅ S ₃ X ₂] ⁺ Cations (E1a) and (E1b) – Compounds with a Distorted Nortricyclane Structure	115
E.5 Conclusion to Chapter E	119
E.6 Experimental Procedures to Chapter E	120
E.7 References to Chapter E	123
Chapter F. Reactions Directed Towards the Synthesis of [As₂X₅]⁺ and [AsX₄]⁺ Salts	127
F.1 Comparison of the Neutral and Cationic Binary E-X Compounds (E = P, As; X = halogen)	127
F.2 Initial Thermodynamic Calculations	128
F.3 Reactions of AsX ₃ , X ₂ and Ag[Al(OR) ₄] (X = Br, I)	130
F.4 Ag ⁺ /EX ₃ /X ₂ Complexes - Reactive Intermediates to [EX ₂] ⁺ , [EX ₄] ⁺ and [E ₂ X ₅] ⁺ Cations	152
F.5 Conclusions to Chapter F	167
F.6 Experimental Procedures to Chapter F	170
F.7 References to Chapter F	179
Chapter G. The Preparation of the [CS₂Br₃]⁺ Carbenium Ion by Oxidation of CS₂ with [AsBr₄]⁺	183
G.1 Introduction to Heteroatom Substituted Carbenium Ion Chemistry	183
G.2 Results	185
G.3 Formation and Electronic Properties of CS ₂ Br ₃ ⁺ Cation	194
G.4 Conclusion to Chapter G	198
G.5 Experimental Procedures to Chapter G	199
Chapter H. The Insertion Reaction of the Long-Lived Cage Phosphenium Ion [P₄S₃I]⁺ Leading to the Novel Spirocyclic [P₇S₆I₂]⁺ Cation	205
H.1 On Cationic P-Y and P-Y-X Cage Compounds (Y = O-Te; X = halogen)	205
H.2 Reactions Leading to the [P ₄ S ₃ I] ⁺ and [P ₇ S ₆ I ₂] ⁺ (H1) Cations	207

H.3 Computational Investigations on the Formation of $[P_4S_3I]^+$ and $[P_7S_6I_2]^+$ (H1)	223
H.4 Conclusion to Chapter H	230
H.5 Preparation Procedures to Chapter H	232
H.6 References to Chapter H	235
Chapter I. Experimental Section	237
I.1 Starting Materials	237
I.2 NMR Spectroscopy	238
I.3 Vibrational Spectroscopy	238
I.4 X-ray Crystallography	238
I.5 Quantum Chemical Calculations	239
I.6 References to Chapter I	240
Chapter J. Conclusion & Outlook	243
Chapter K. Appendix	253
K.1 Crystal Structure Tables	253
K.2 Supplementary Figures of Solid State Structures	260
K.3 Supplementary Structures of Calculated Species (not included in the main text)	263
K.4 Computational Data of All Calculated Species	265
K.5 Selected Relevant NMR Spectra	272
K.6 Miscellaneous	283
K.7 List of Publications and Conference Contributions	284
Chapter L. Curriculum Vitae	287