

---

# Inorganic Reactions and Methods

---

## Volume 9

The Formation of Bonds to C, Si, Ge, Sn, Pb  
(Part 1)

---

Founding Editor

**J.J. Zuckerman**

---

Editor

**A.P. Hagen**

---



# Contents of Volume 9

How to use this book	xiii
Preface to the Series	xix
Editorial Consultants to the Series	xxiii
Contributors to Volume 9	xxv

<b>5.</b>	<b>Formation of the Bonds to the Group-IVB (C, Si, Ge, Sn, Pb) Elements</b>	<b>1</b>
<b>5.1.</b>	<b>Introduction</b>	<b>2</b>
<b>5.2.</b>	<b>Formation of the Group-IVB (C, Si, Ge, Sn, Pb)–Group-IVB (C, Si, Ge, Sn, Pb) Element Bond</b>	<b>3</b>
5.2.1.	Introduction	3
5.2.2.	Formation of the Carbon–Carbon Bond	3
5.2.3.	Formation of the Si—Si Bond	3
5.2.3.1.	in Elemental Silicon	3
5.2.3.1.1.	from Oxides.	3
5.2.3.1.2.	by Other Methods.	4
5.2.3.1.3.	Formation of High-Purity Silicon	4
5.2.3.1.4.	Electrochemical Formation of Compounds with Si—Si Bonds (Including Elemental Silicon)	6
5.2.3.2.	from Metal Silicides	7
5.2.3.2.1.	by Solvolysis in Aqueous or Liquid Ammonia Solutions.	7
5.2.3.2.2.	Formation of Oligosilanes	8
5.2.3.2.3.	Formation of Polymeric Compounds	9
5.2.3.3.	from Silicon Hydrides and Organosilicon Hydrides	11
5.2.3.3.1.	by the Action of a Silent Electric Discharge.	11
5.2.3.3.2.	by Direct Photolysis.	11

5.2.3.3.3.	by Sensitized Photolysis.	13
5.2.3.3.4.	by Catalyzed Reactions.	15
5.2.3.3.5.	by Reaction with Silylmetallic Compounds.	17
5.2.3.4.	from Silicon Halides and Organosilicon Halides	17
5.2.3.4.1.	by Electrochemical Reduction.	17
5.2.3.4.2.	by Halide Elimination with Active Metals.	18
5.2.3.4.3.	by Reaction with Silylmetallics.	20
5.2.3.4.4.	by Catalyzed Disproportionation.	22
5.2.3.4.5.	by Reaction with Organomagnesium Halide Reagents.	23
5.2.3.4.6.	by the Action of Silent Electric Discharge.	24
5.2.3.4.7.	by Mercury-Photosensitized Photolyses.	24
5.2.3.5.	from Bissilylmercury Compounds	25
5.2.3.5.1.	by Thermolysis.	25
5.2.3.5.2.	by Photolysis.	26
5.2.3.6.	from Organosilanes and Silicon Halides by Hydrogenolysis.	26
5.2.3.7.	from Silylenes	28
5.2.3.7.1.	by Oligomerization.	28
5.2.3.7.2.	by Insertions into Bonds of Silicon to Hydrogen, Oxygen and Silicon.	29
5.2.3.7.3.	by Addition to Si=C.	33
5.2.3.8.	in the Direct Reaction of Methyl Chloride with Silicon-Copper.	33
5.2.4.	Formation of the Germanium-Germanium Bond	34
5.2.4.1.	in Elemental Germanium	34
5.2.4.1.1.	from Oxides.	35
5.2.4.1.2.	from Sulfides.	39
5.2.4.1.3.	by Other Syntheses.	39
5.2.4.1.4.	Formation of High-Purity Germanium.	43
5.2.4.2.	from Organogermanium Hydrides	45
5.2.4.2.1.	by Reaction with Diorganomercury Compounds in the Presence of UV Radiation.	45
5.2.4.2.2.	by Hydrogermolysis Reaction.	46
5.2.4.2.3.	by Germanium Hydride Decomposition.	48
5.2.4.3.	from Ge(IV) Halides and Organogermanium(IV) Halides	49
5.2.4.3.1.	by the Action of a Microwave Discharge of Ge(IV) Halides.	49
5.2.4.3.2.	by Electrochemical Reduction.	49
5.2.4.3.3.	by Halide Elimination with Active Metals.	52
5.2.4.3.4.	by Reaction with Germyl-Metal Reagents.	55

5.2.4.3.5.	by Reaction with Organometallic Reagents.	59
5.2.4.4.	from Germanium(II) Halides	61
5.2.4.4.1.	by Reactions with Germyl-Metal Reagents.	61
5.2.4.4.2.	by Reaction with Organometallic Reagents.	62
5.2.4.5.	from Germyl Compounds of Cadmium, Mercury, Thallium, Antimony and Bismuth	64
5.2.4.5.1.	by Thermolysis or Photolysis.	64
5.2.4.6.	from Germylenes	66
5.2.4.6.1.	by Oligomerization of Germylenes.	66
5.2.4.6.2.	by Insertions into Bonds of Germanium to Hydrogen, Halogen, Carbon, Oxygen, Sulfur, Nitrogen, Phosphorus and Germanium.	68
5.2.5.	The Formation of the Tin—Tin Bond	73
5.2.5.1.	in Elemental Tin	73
5.2.5.1.1.	from Oxides.	73
5.2.5.1.2.	from Sulfides.	75
5.2.5.1.3.	by Other Syntheses.	75
5.2.5.1.4.	Allotropy of Tin	76
5.2.5.2.	from Organotin Hydrides	77
5.2.5.2.1.	by Catalytic Hydrogen Elimination.	77
5.2.5.2.2.	by Reaction with Organotin Halogen, Pseudohalogen, Chalcogen and Pnictogen Compounds.	79
5.2.5.2.3.	by Reaction with Organometallic Compounds.	82
5.2.5.2.4.	by Reaction with Reducible Organic Compounds.	83
5.2.5.3.	from Organotin Halides	84
5.2.5.3.1.	by Electrochemical Reduction.	84
5.2.5.3.2.	by Halide Elimination with Active Metals.	85
5.2.5.3.3.	by Reaction with Stannyl Metal Reagents.	86
5.2.5.3.4.	by Reactions with Bulky Organometallic Reagents.	88
5.2.5.4.	from Tin(II) Halides by Reaction with Organometallic Reagents.	89
5.2.5.5.	from Bis(stannyl) Compounds of Mercury.	90
5.2.5.6.	from Stannylenes	93
5.2.5.6.1.	by Oligomerization of Stannylenes.	93
5.2.5.6.2.	by Insertions into Bonds of Tin to Hydrogen, Carbon and Tin.	94
5.2.5.7.	from Sodium-Tin Alloys by Reaction with Organic and Organometallic Compounds.	95

5.2.6.	Formation of the Lead–Lead Bond	96
5.2.6.1.	in Metallic Lead	96
5.2.6.1.1.	from Oxides.	97
5.2.6.1.2.	from Sulfides.	97
5.2.6.1.3.	by Other Syntheses.	98
5.2.6.2.	from Lead(II) and Lead(IV) Salts by Reaction with Organometallic Reagents.	99
5.2.6.3.	from Organolead Hydrides	101
5.2.6.3.1.	by Thermolysis and Photolysis.	101
5.2.6.4.	from Organolead Halides	101
5.2.6.4.1.	by Halide Elimination with Active Metals.	101
5.2.6.4.2.	by Reaction with Plumbyl – Metal Reagents.	102
5.2.6.5.	from Organolead Hydroxides by Electrolysis.	102
5.2.6.6.	from Lead Alloys	103
5.2.6.6.1.	by Reaction with Organic Halides.	103
5.2.6.6.2.	by Reaction with Cryptate Reagents.	103
5.2.6.7.	by Other Syntheses	104
5.2.6.7.1.	by Oxidation Processes.	104
5.2.6.7.2.	by Reductive Processes.	104
5.2.7.	The Formation of the Carbon–Silicon Bond	105
5.2.7.1.	from the Elements.	105
5.2.7.2.	from Elemental Silicon and Its Alloys	105
5.2.7.2.1.	by Reaction with Alkyl Halides.	105
5.2.7.2.2.	by Reaction with Aryl Halides.	110
5.2.7.2.3.	by Reaction with Other Species.	112
5.2.7.3.	from Silicon Halides	113
5.2.7.3.1.	by Reaction with Active Organometallics.	113
5.2.7.3.2.	by Interaction with Organic Halides with Active Metals.	138
5.2.7.3.3.	by Interaction with Unsaturated Organic Derivatives and Active Metals.	143
5.2.7.3.4.	by Redistribution Reactions with Organosilanes.	159
5.2.7.3.5.	by Reaction with Hydrocarbons.	161
5.2.7.3.6.	by Reaction with Diazoalkanes.	162
5.2.7.4.	from Silicon Alkoxides, Silicon Carboxylates or Siloxanes	163
5.2.7.4.1.	by Reaction with Active Organometallics.	163
5.2.7.4.2.	by Interaction with Organic Halides and Active Metals.	170
5.2.7.4.3.	by Interaction with Unsaturated Organic Compounds.	173

5.2.7.5.	from Silicon Hydrides	176
5.2.7.5.1.	by Addition to Olefinic or Acetylenic Linkages.	176
5.2.7.5.2.	by Reaction with Diazoalkanes or Other Carbenoids.	180
5.2.7.5.3.	by Reaction with Active Organometallics to Eliminate MH.	182
5.2.7.5.4.	from the Pyrolysis of Organohydrosilanes.	185
5.2.7.6.	from Silylmetallics	185
5.2.7.6.1.	by Reaction with Organic Halides to Eliminate MX.	186
5.2.7.6.2.	by Cleavage of Certain Ethers and Epoxides.	195
5.2.7.6.3.	by Addition to Carbonyl Groups of CO <sub>2</sub> and Other Acyl Derivatives.	198
5.2.7.6.4.	by Addition to C—C Unsaturated Systems.	202
5.2.7.7.	from Other Organosilanes by Exchange with Active Organometallics.	207
5.2.8.	Formation of the Carbon–Germanium Bond	212
5.2.8.1.	from the Elements.	212
5.2.8.2.	from Elemental Germanium and Its Alloys	212
5.2.8.2.1.	by Reaction with Alkyl Halides.	212
5.2.8.2.2.	by Reaction with Aryl Halides.	215
5.2.8.3.	from Germanium Halides (Di- and Tetravalent)	216
5.2.8.3.1.	by Reaction with Active Organometallics.	217
5.2.8.3.2.	by Interaction with Organic Halides and Active Metals.	224
5.2.8.3.3.	by Addition of Organic Halide to Germanium(II) Halides and Organohalogermylenes.	227
5.2.8.3.4.	by Addition of Germylenes to Unsaturated Compounds.	228
5.2.8.3.5.	by Redistribution Reactions with Organogermanes.	232
5.2.8.3.6.	by Reaction with Diazoalkanes.	234
5.2.8.4.	from Germanium Alkoxides, Germanium Carboxylates or Germanium Oxides	236
5.2.8.4.1.	by Reaction with Active Organometallics.	237
5.2.8.4.2.	by Reaction with Organic Halides and Active Metals.	239
5.2.8.5.	from Germanium Hydrides	240
5.2.8.5.1.	by Addition to Olefinic or Acetylenic Linkages.	240

5.2.8.5.2.	by Reaction with Diazoderivatives or Other Carbenoides.	252
5.2.8.5.3.	by Reaction with Active Organometallics to Eliminate MH.	254
5.2.8.6.	from Germylmetallics	256
5.2.8.6.1.	by Reaction with Organic Halides to Eliminate HX	257
5.2.8.6.2.	by Reaction with Ethers.	261
5.2.8.6.3.	by Addition to the Carbonyl Group of CO <sub>2</sub> and Other Acyl Derivatives.	262
5.2.8.6.4.	by Addition to Alkenes and Alkynes.	264
5.2.8.7.	from Other Organogermanes by Exchange with Active Organometallics	266
5.2.9.	Formation of the Carbon-Tin Bond	268
5.2.9.1.	from the Elements.	268
5.2.9.2.	from the Metal and Its Alloys	269
5.2.9.2.1.	by Reaction with Alkyl Halides.	269
5.2.9.2.2.	by Reaction with Alkyl Halides Having Alkenyl or Aryl Substituents	272
5.2.9.2.3.	by Reaction with Alkyl Halides Having Other Substituents.	273
5.2.9.2.4.	by Electrolysis at a Tin Anode.	276
5.2.9.2.5.	by Electrolysis at a Tin Cathode.	277
5.2.9.3.	from Tin Halides (Di- and Tetravalent)	278
5.2.9.3.1.	by Reaction with Active Organometallics.	278
5.2.9.3.2.	Redistribution Reactions Involving Tetraorganostannanes and Tin(IV) Halides.	311
5.2.9.3.3.	from Tin(II) Halides.	317
5.2.9.3.4.	by Reaction with Diazoalkanes.	322
5.2.9.3.5.	by Reaction with Another Carbon-Centered Protic Compound.	323
5.2.9.4.	from Tin Alkoxides, Tin Carboxylates or Tin Oxides	324
5.2.9.4.1.	by Reaction with Active Organometallics.	324
5.2.9.4.2.	by Reaction with Terminal Acetylenes.	327
5.2.9.4.3.	by Decarboxylation of Organotin Carboxylates and Other Elimination Reactions.	328
5.2.9.4.4.	by Addition to Carbon-Carbon Multiple Bonds.	329
5.2.9.4.5.	by Transesterification.	331
5.2.9.5.	from Tin Hydrides	332
5.2.9.5.1.	by Hydrostannation of Alkenes.	333
5.2.9.5.2.	by Hydrostannation of Alkynes.	345

5.2.9.5.3.	by Formation of Heterocyclic Compounds by Hydrostannation.	350
5.2.9.5.4.	by Reaction with Diazoalkanes.	352
5.2.9.6.	from Organotin Amides	353
5.2.9.6.1.	by Insertion.	355
5.2.9.6.2.	by Reaction with a Terminal Acetylene.	356
5.2.9.6.3.	by Reaction with a Cyclopentadiene.	357
5.2.9.6.4.	by Reaction with a Diazoalkane.	357
5.2.9.6.5.	by Reaction with Another Carbon-Centered Protic Compound.	358
5.2.9.7.	from Stannylmetallics	359
5.2.9.7.1.	by Reaction with Organic Halides to Eliminate MX.	360
5.2.9.7.2.	by Addition to Alkenes and Alkynes	365
5.2.9.7.3.	by Cleavage of Ethers and Epoxides.	367
5.2.9.8.	from Other Organotins by Exchange with Active Organometallics.	367
5.2.10.	Formation of the Carbon – Lead Bond	370
5.2.10.1.	from the Elements	370
5.2.10.2.	from Lead Metal and Its Alloys	370
5.2.10.2.1.	by Reaction with Alkyl Halides and Alkyl Esters.	370
5.2.10.2.2.	by Reaction with Aryl Halides	375
5.2.10.2.3.	by Reaction with Other Species	376
5.2.10.2.4.	by Electrolysis of Sodium Tetraorganoaluminates at a Lead Anode	377
5.2.10.2.5.	by the Action of Aryldiazonium Salts on Pb Metal	379
5.2.10.3.	from Lead Halides (Di- and Tetravalent)	380
5.2.10.3.1.	by Reaction with Active Organometallics	380
5.2.10.3.2.	by Interaction of Lead(II) Salts with an Active Organometallic and an Organic Halide	387
5.2.10.4.	from Lead(II) Oxide, Lead Carboxylate or Plumbite Salts	389
5.2.10.4.1.	by Reaction of an Organic Halide with Sodium Plumbite.	389
5.2.10.4.2.	by Reaction with an Active Organometallic	389
5.2.10.5.	from Organolead Hydrides	394
5.2.10.6.	from Organolead Amides	396
5.2.10.7.	from Plumbylmetallics	397
5.2.10.7.1.	by Reaction with Organic Halides To Eliminate MX.	397
5.2.10.7.2.	by Addition to Alkenes and Alkynes.	400
5.2.10.7.3.	by Cleavage of Epoxides and Lactones.	400



---

5.2.10.8.	from Other Organoleads by Exchange with Active Organometallics.	400
5.2.11.	Formation of Mixed Group-IVB–Group-IVB Element Bonds (Except Carbon–Group-IVB Bonds)	404
5.2.11.1.	from the Elements	405
5.2.11.1.1.	in Alloys.	405
5.2.11.1.2.	in Silicides.	405
5.2.11.1.3.	in Germanides.	406
5.2.11.1.4.	in Hydrides.	406
5.2.11.2.	from Group IVB Halides (Di- and Tetravalent)	407
5.2.11.2.1.	by Halide Elimination with Active Metals.	407
5.2.11.2.2.	by Reaction with a Group-IVB Element–Active Metal Reagent	407
5.2.11.3.	from Group-IVB Hydrides	408
5.2.11.3.1.	by Reaction with a Group-IVB Element–Active Metal Reagent.	408
5.2.11.3.2.	by Reaction with a Group-IVB Element Amide.	409
5.2.11.4.	from Group-IVB Alkoxides and Carboxylates by Reaction with a Group-IVB Element–Active Metal Reagent.	409
5.2.11.5.	from Mixed Group-IVB Element Mercurials, by Photolysis	410
5.2.11.6.	by Insertion of Silylenes, Germylenes, Stannylenes and Plumbylenes into Group-IVB–Hydrogen, –Halide and –Carbon Bonds.	410
List of Abbreviations		411
Author Index		417
Compound Index		465
Subject Index		599