
Inorganic Reactions and Methods

Volume 11

**Formation of Bonds to C, Si,
Ge, Sn, Pb (Part 3)**

Editor

J.J. Zuckerman

Subject Index Editor

A.P. Hagen



Contents of Volume 11

How to Use this Book	xi
Preface to the Series	xvii
Editorial Consultants to the Series	xxi
Contributors to Volume 11	xxiii

5.	The Formation of Bonds to Elements of Group IVB (C, Si, Ge, Sn, Pb) (Part 3)	1
5.5.	Formation of Bonds between Elements of Groups IVB (C, Si, Ge, Sn, Pb) and IA (Li, Na, K, Rb, Cs, Fr)	2
5.5.1.	Introduction	2
5.5.2	Carbon–Lithium Bonds	2
5.5.2.1	from the Elements.	2
5.5.2.2.	from Lithium and its Alloys	3
5.5.2.2.1.	with Organic Halides.	3
5.5.2.2.2.	with Organomercurials.	14
5.5.2.2.3.	with Adducts of Conjugated Hydrocarbons in Donor Solvents.	17
5.5.2.2.4.	with Acidic Hydrocarbons Evolving H ₂ .	26
5.5.2.2.5	with Ethers, Amines, Sulfides and Phosphines Cleaving the Carbon–Element Bonds.	28
5.5.2.3.	from Other Organolithiums	31
5.5.2.3.1.	by Metal–Metal Exchange with Less Active Organometallics.	35
5.5.2.3.2.	by Proton–Metal Exchange with Acidic C—H Bonds.	44
5.5.2.3.3.	by Halogen–Lithium Exchange with Organic Halides.	107
5.5.2.3.4.	by Addition of Organolithiums to Olefins or Acetylenes.	129
5.5.2.3.5.	by Action of Lithium Arene Radical Anions and Dianions.	142

5.5.3.	Carbon–Group-IA Bonds	148
5.5.3.1.	from the Elements	148
5.5.3.1.1.	Giving Na Carbides.	148
5.5.3.1.2.	Giving K, Rb and Cs Carbides.	148
5.5.3.2.	from the Group-IA Metals and Their Alloys	149
5.5.3.2.1.	with Organic Halides.	149
5.5.3.2.2.	with Ethers.	153
5.5.3.2.3.	with Organomercurials.	158
5.5.3.2.4.	with Adducts of Conjugated Hydrocarbons in Donor Solvents.	160
5.5.3.2.5.	with Acidic Hydrocarbons Evolving H ₂ .	164
5.5.3.2.6.	by Cleavage of Carbon–Carbon Bonds.	167
5.5.3.3.	from Other Group-IA Organometallics of the Same Metal	171
5.5.3.3.1.	by Proton–Metal Exchange with Acidic C–H Bonds.	171
5.5.3.3.2.	by Metal–Metal Exchange with Less Active Organometallics.	175
5.5.3.3.3.	by Addition to Olefins and Acetylenes.	176
5.5.4.	Silicon–Group-IA Bonds	177
5.5.4.1.	from the Elements.	177
5.5.4.2.	from Organodi- and Organopolysilanes	178
5.5.4.2.1.	with Alkali Metals.	178
5.5.4.2.2.	with Anionic Reagents.	181
5.5.4.3.	from Organohalosilanes with Alkali Metals.	183
5.5.4.4.	from Organosilicon Hydrides with Alkali Metals and Metal Hydrides.	185
5.5.4.5.	from Tetraorganosilanes with Alkali Metals.	185
5.5.4.6.	from Silylmercurials.	186
5.5.4.7.	from Exchange.	187
5.5.5.	Germanium–Group-IA Bonds	187
5.5.5.1.	from the Elements.	188
5.5.5.2.	from Organodigermans	188
5.5.5.2.1.	with Alkali Metals.	188
5.5.5.2.2.	with Alkali-Metal Alkoxides and Organolithiums.	191
5.5.5.3.	from Organohalogermanes with Alkali Metals.	191
5.5.5.4.	from Organogermanium Hydrides with Alkali Metals and Derivatives.	192
5.5.5.5.	from Tetraorganogermanes with Alkali Metals.	194
5.5.5.6.	from Germy–Mercury and –Thallium with Alkali Metals.	195
5.5.5.7.	from Exchange and/or Ge(II) Derivatives.	197
5.5.6.	Tin–Group-IA Bonds	197
5.5.6.1.	from the Elements	199
5.5.6.1.1.	Lithium.	199

5.5.6.1.2.	Sodium.	199
5.5.6.1.3.	Potassium.	200
5.5.6.1.4.	Rubidium.	200
5.5.6.1.5.	Cesium.	200
5.5.6.2.	from Organodistannanes with Alkali Metals	200
5.5.6.2.1.	Lithium.	200
5.5.6.2.2.	Sodium.	202
5.5.6.2.3.	Potassium.	203
5.5.6.3.	from Organotin Halides with Alkali Metals	203
5.5.6.3.1.	Lithium.	203
5.5.6.3.2.	Sodium.	204
5.5.6.3.3.	Potassium.	204
5.5.6.4.	from Organotin Hydrides with Alkali Metals.	205
5.5.6.5.	from Tetraorganotins with Alkali Metals.	205
5.5.6.6.	from Tin(II) Compounds with Organoalkali Reagents.	206
5.5.7.	Lead–Group-IA Bonds	207
5.5.7.1.	in Alloys and Intermetallics	207
5.5.7.1.1.	from the Elements.	207
5.5.7.1.2.	by Reduction.	209
5.5.7.1.3.	by Electrolysis.	209
5.5.7.2.	from Hexaorganodiplumbanes.	210
5.5.7.2.1.	with Alkali Metals.	210
5.5.7.2.2.	with Organoalkali Reagents.	212
5.5.7.3.	from Tetraorganoleads with Alkali Metals.	212
5.5.7.4.	from Organolead Halides with Alkali Metals.	213
5.5.7.5.	from Lead(II) Compounds with Organoalkali Reagents.	214
5.5.7.6.	by Miscellaneous Routes.	214

5.6. Formation of Bonds between Elements of Group IVB (C, Si, Ge, Sn, Pb) and Group IB (Cu, Ag, Au) 215

5.6.1.	Introduction	215
5.6.2.	from the Elements.	215
5.6.3.	from the Group-IB Metals and Alloys.	216
5.6.4.	from the Metal Salts	217
5.6.4.1.	by Metal–Metal Exchange with Another Organometallic.	219
5.6.4.2.	by Metal–Halogen Exchange.	229
5.6.4.3.	by Metallation.	229
5.6.4.4.	by Insertion.	233
5.6.4.5.	by Addition, Decarboxylation.	234
5.6.4.6.	by Forming Adducts with Unsaturated Hydrocarbons.	235

5.6.5.	From the Metal–Phosphine Complexes	236
5.6.5.1.	with Triaryl Group IV–Alkali-Metal Derivatives.	236
5.6.5.2.	by Insertion.	237
5.6.5.3.	by Transmetallation.	237
5.6.5.4.	by Metal–Halide Exchange.	237

5.7**Formation of Bonds between Elements of Group IVB (C, Si, Ge, Sn, Pb) and Group IIB (Zn, Cd, Hg)****238**

5.7.1.	Introduction	238
5.7.2.	Carbon–Group-IIB Bonds	238
5.7.2.1.	from the Elements.	238
5.7.2.2.	from the Group-IIB Metals and Alloys	238
5.7.2.2.1.	with Organic Halides and Sulfates.	238
5.7.2.2.2.	with Organomercurials.	247
5.7.2.2.3.	with Aryldiazonium Salts.	248
5.7.2.3.	from Metal Salts	248
5.7.2.3.1.	with Organometallics.	248
5.7.2.3.2.	by Redistribution with the Organometallics of the Same Metal.	270
5.7.2.3.3.	by Addition to Olefins and Acetylenes or Cyclopropanes by Ring Opening.	277
5.7.2.3.4.	with Acidic Hydrocarbons.	302
5.7.2.3.5.	with Diazoalkanes.	318
5.7.2.3.6.	with Diazonium Salts.	320
5.7.2.3.7.	with Organosulfinic, Organosulfonic and Organoboronic Acid Derivatives.	323
5.7.2.4.	from Other Group-IIB Organometallics of the Same Metal	335
5.7.2.4.1.	by Proton–Metal Exchange with Acidic Hydrocarbons.	336
5.7.2.4.2.	by Olefin Insertion.	337
5.7.2.4.3.	by Metal–Metal Exchange with Other Organometallics.	339
5.7.3.	Silicon–Group-IIB Bonds	340
5.7.3.1.	from Silyl–Alkali-Metal Reagents with Group-IIB Halides and Organohalides.	342
5.7.3.2.	from Organohalosilanes with Na or Al Amalgam.	343
5.7.3.3.	from Organosilicon Hydrides with Zn, Cd and Hg Dialkyls.	344
5.7.3.4.	from Silylcadmiums and -Thalliums with Hg Metal.	346
5.7.3.5.	from Redistribution and Related Reactions.	346

5.7.4.	Ge—Group-IIB Bonds	347
5.7.4.1.	from Germyl—Alkali-Metal Reagents with Group-IIB Halides and Organohalides.	348
5.7.4.2.	from Organogermanium Hydrides with Zn, Cd and Hg Dialkyls.	348
5.7.4.3.	from Organohalogermanes with Na Amalgam.	351
5.7.4.4.	from Germylcadmiums, -thalliums and -bismuths with Hg.	352
5.7.4.5.	from Digermanes with Hg(II) Compounds.	352
5.7.4.6.	from Germyl—Group-IIB Compounds by Redistribution.	353
5.7.4.7.	from Silyl- or Germylmercurials and Ge(IV) Halides.	354
5.7.4.8.	by Insertion of Germylenes into Hg—C or Hg—Ge Bonds.	354
5.7.5.	Tin—Group-IIB Bonds	355
5.7.5.1.	from the Elements	356
5.7.5.1.1.	with Zn.	356
5.7.5.1.2.	with Cd.	357
5.7.5.1.3.	with Hg.	357
5.7.5.2.	from Organotin Hydrides with Zn, Cd and Hg Dialkyls	358
5.7.5.2.2.	with CD Alkyls.	359
5.7.5.2.3.	with Hg Alkyls.	360
5.7.5.3.	from Organotin Halides with Germylmercurials.	362
5.7.5.4.	from Organotin Alkoxides with Silylmercurials.	363
5.7.6.	Lead—Group-IIB Bonds	364
5.7.6.1.	in Alloys and Intermetallics	364
5.7.6.1.1.	from the Elements.	364
5.7.6.1.2.	by Reduction.	364
5.7.6.1.3.	by Electrolysis.	365
5.7.6.2.	in Organolead—Group-IIB Compounds.	365