

Contents

1	Introduction	1
1.1	Synthesis of C-Substituted Carboranes	2
1.1.1	Reaction of Decaborane with Acetylenes	2
1.1.2	Reaction of Lithiocarborane with Electrophiles	3
1.1.3	Reaction of Carboranylcopper	5
1.1.4	Other Methods	7
1.2	Synthesis of B-Substituted Carboranes	8
1.2.1	Reaction of Decaborane with Acetylenes	8
1.2.2	Electrophilic Substitution of Carboranes	8
1.2.3	Reaction of Dicarbollide Ion ($C_2B_9H_{11}^{2-}$) with Dihalobarane	9
1.2.4	Transition Metal-Catalyzed Coupling Reaction	10
1.2.5	Carbene Reaction	12
1.2.6	Other Methods	12
1.3	1,2- <i>o</i> -Carboryne	13
1.4	Transition Metal-1,2- <i>o</i> -Carboryne Complexes	16
1.4.1	Synthesis of Transition Metal-1,2- <i>o</i> -Carboryne Complexes	17
1.4.2	Reactivity of Zr-1,2- <i>o</i> -Carboryne Complexes	20
1.4.3	Reactivity of Ni-1,2- <i>o</i> -Carboryne Complexes	24
1.5	Our Objectives	25
	References	26
2	Nickel-1,2-<i>o</i>-Carboryne Complexes	31
2.1	Introduction	31
2.2	Synthesis and Structure of B-Substituted Nickel-1,2- <i>o</i> -Carboryne Complexes	32
2.3	Summary	36
	References	36

3	Nickel-Mediated Coupling Reaction of 1,2-<i>o</i>-Carboryne with Alkenes	39
3.1	Introduction	39
3.2	Results and Discussion	40
3.3	Summary	53
	References	54
4	Nickel-Mediated/Catalyzed Three-Component Cycloaddition Reaction of 1,2-<i>o</i>-Carboryne/Arynes, Alkenes, and Alkynes	55
4.1	Introduction	55
4.2	Results and Discussion	56
4.3	Summary	68
	References	68
5	Nickel-Catalyzed [2+2+2] Cycloaddition of 1,2-<i>o</i>-Carboryne with Alkynes	71
5.1	Introduction	71
5.2	Results and Discussion	71
5.3	Summary	82
	References	82
6	Palladium/Nickel-Cocatalyzed [2+2+2] Cycloaddition of 1,3-<i>o</i>-Carboryne with Alkynes	85
6.1	Introduction	85
6.2	Results and Discussion	86
6.2.1	Synthesis of 1,3- <i>o</i> -Carboryne Precursor	86
6.2.2	Reaction of 1,3- <i>o</i> -Carboryne Precursor	87
6.2.3	Metal-Catalyzed [2+2+2] Cycloaddition of 1,3- <i>o</i> -Carboryne with Alkynes	88
6.2.4	Proposed Mechanism	92
6.3	Summary	95
	References	95
7	Conclusion	99
8	Experimental Section	101
	References	126
	Appendix	129

Late Transition Metal-Carbonyne Complexes
Synthesis, Structure, Bonding, and Reaction with
Alkenes and Alkynes

Qiu, Z.

2012, XVIII, 134 p., Hardcover

ISBN: 978-3-642-24360-8