

CONTENTS

PREFACE	vii
✓ 1. CARBON-METAL BONDING. <i>James W. Richardson</i>	1
Introduction	1
Single Bonds. Polar and Nonpolar	2
MO Description of HeH^+	2
The Antibonding Wave Function	4
Correlation Diagram	5
Octahedral Transition-Metal Complexes.	6
Orbitals for Octahedral Complexes	7
Complexes With Simple Ligands	7
Unsaturated Ligands— $\text{Fe}(\text{CN})_6^{-4}$	10
Carbonyl Compounds.	12
Correlation Diagram for $\text{Ni}(\text{CO})_4$	12
Sigma Bonding Systems	14
Pi Bonding Systems	15
Charge Distribution in $\text{Ni}(\text{CO})_4$	16
Bond Orders in $\text{Ni}(\text{CO})_4$	18
Bis-Cyclopentadienyl Compounds.	20
Orbitals for Bis-Cyclopentadienyl Compounds	21
Correlation Diagram and Bond Properties	22
Magnetic Properties.	25
Charge Distributions	26
Representation of Bonding by "Equivalent Orbitals"	26
Stability of Alkyl and Aryl Transition-Metal Compounds.	28
Review	28
Comparison of Methyl and Halogen Bonding	29
Conditions for Stability.	32
Conclusion	34
2. BENZYNE CHEMISTRY. <i>Rolf Huisgen</i>	36
Benzyne Type Intermediates in Nucleophilic Aromatic Substitutions	36
History and Formulation of Benzyne	37
Evidence from Rearrangements in Nucleophilic Aromatic Substitutions	38
The Mechanism of Aryne Formation	51
Two-step Reaction in Liberation of Benzyne with Organolithium Compounds.	52

The Reaction of Halobenzenes with Alkali Amide in Liquid Ammonia	54
Kinetics of the Reaction of Halobenzenes with Lithium Piperidide in Ether	55
Rate and Nature of the Metalating Agent	58
Rate and Nature of the Aryl Group	60
Other Routes to Arynes	62
Relation to Other Eliminations	63
Typical Reactions of Arynes	65
Phenylation of Carbanions.	65
Benzyne as Dienophile	66
Ring Closure Reactions	68
Catalytic Arylation of Aryl Chlorides	71
Quantitative Data from Competition Experiments and the Nature of Arynes.	73
Characterization of Benzyne as Intermediate	73
Selectivity Differences of Arynes	74
The Nucleophilicity Scale towards Aryne as Reference Acid	76
Orientation in Addition to Arynes	78
Structure of Benzyne	81
3. VINYLMETALLICS, <i>H. D. Kaesz and F. G. A. Stone</i>	88
Introduction	88
Vinyl Compounds of Alkali Metals and Magnesium	89
Alkali Metals.	89
Magnesium.	91
Vinyl Compounds of the Group IIb Metals	92
Vinyl Compounds of the Group III Elements	102
Boron	103
Aluminum	113
Thallium	114
Silicon.	115
Germanium	118
Tin.	121
Lead.	127
Vinyl Compounds of the Group V Elements.	128
The Infrared Spectra of Some Vinyl Compounds	136
4. ORGANOBORANES, <i>Herbert C. Brown</i>.	150
Introduction	150
Synthesis of Organoboranes <i>via</i> Organometallics	151
Hydroboration	152
Early Observations	152

Experimental Procedures.	156
Scope and Stoichiometry.	158
Directive Effects.	160
Bis-3-methyl-2-butylborane as a Selective Hydroborating Agent . . .	164
Cyclic Olefins. Stereochemistry of Hydroboration	166
Hydroboration of Dienes	169
Hydroboration of Acetylenes	170
Reactions of Organoboranes	171
Thermal Behavior.	171
Isomerization	173
Displacement Reactions	177
Redistribution Reactions.	181
Protonolysis	182
Mercuration	184
Oxidation.	184
Addition Compounds of Organoboranes.	186
Conclusion	189
5. ORGANO-ALUMINUM COMPOUNDS, <i>Karl Ziegler</i>	194
Introduction	194
Synthesis and Classification of Organo-Aluminum Compounds	194
The New "Direct Synthesis" of Aluminum Trialkyls	194
Other Routes to Organo-Aluminum Compounds	197
Different Types of Organo-Aluminum Compounds with Three Substituents Bound to Aluminum.	198
Coordination Complexes of Organo-Aluminum Compounds	199
Interconversion of Organo-Aluminum Compounds	202
Molecular Structure and Properties of Organo-Aluminum Com- pounds.	207
Organo-Aluminum Compounds and Intermolecular Forces	207
Spectroscopic and Miscellaneous Physical Properties of Organo- Aluminum Compounds.	212
Reactions of Organo-Aluminum Compounds	214
Introduction	214
Reactions in which the Sum of Al—C + Al—H Bonds (+ Free Al) Remains Constant.	215
Reactions of Organo-Aluminum Compounds with Cleavage of Al—C and Al—H Bonds.	236
Reactions in which Al—C Bonds Are Broken but Total Number of Metal-Carbon Bonds Remains Constant (Synthesis of Other Metal Alkyls).	242
Electrolysis of Organo-Aluminum Compounds	251

6. ORGANOSILYLMETALLIC CHEMISTRY, <i>Henry Gilman and Hans J. S. Winkler</i>	270
Historical Review	270
Preparation of Organosilylmetallic Compounds.	272
Metal Cleavage of Bond between Silicon and Hydrogen	273
Metal Cleavage of Bond between Silicon and Silicon	274
Metal Cleavage of Bond between Silicon and Group IV Elements other than Silicon	277
Metal Cleavage of Bond between Silicon and Group VI Elements.	280
Metal Cleavage of Bond between Silicon and Group VII Elements	281
Analytical Chemistry of Organosilylmetallic Compounds	286
Reactions of Organosilylmetallic Compounds.	287
With Elements.	287
With Inorganic Compounds.	288
With Organic Compounds.	291
Comparison Between Organosilylmetallic and Organogermylemetallic Chemistry.	331
Reactivity of Organosilylmetallic Compounds.	335
7. CYCLOPENTADIENYL METAL COMPOUNDS, <i>P. L. Pauson</i>	346
Introduction	346
Compounds with Two Hydrocarbon Ligands	346
Compounds with One Hydrocarbon Ligand	350
Preparation of Dicyclopentadienylmetal Derivatives.	355
Some Properties and Structures	359
Reactions not Involving the Cyclopentadienyl Group.	363
Aromatic Substitution Reactions	364
Friedel-Crafts Acylation	365
Sulfonation	367
Mercuration	367
Arylation	369
Condensation with Formaldehyde	369
Aldehydes	369
Metalation	371
8. ARENE COMPLEXES OF THE TRANSITION METALS, <i>H. Zeiss</i>	380
Introduction	380
Hein's Polyphenylchromium Chemistry	381
Origin of the π -Bis-Arene Concept	383
Experimental Basis	383
Onsager's Proposal	386
Bis-Arene Chromium	388
Fischer-Hafner Synthesis.	388

Properties of Bis-Benzene-Chromium	389
Grignard Synthesis	392
Triphenylchromium Synthesis	392
Bis-Arene Metal Complexes	397
Arene Complexes of V and Fe	397
Bis-Arene Complexes of Re, Ru, Os, Co, Rh, and Ir	405
Acetylenic Synthesis of Cr, Mn, and Co Bis-Arene Complexes	406
Mixed Arene and Arene Carbonyl Metal Complexes	407
Nonbenzenoid Arene Metal Complexes	408
Heterocyclic Metal Complexes	410
Acetylenic Metal Complexes	411
Cyclic Condensation on Chromium	411
Cyclic Condensation on Nickel	414
Cyclic Condensation on Cobalt	415
Addition Reactions	416
The Job-Cassal Reaction	417
9. TRANSITION METAL ALKYLs AND ARYLs. <i>G. E. Coates and F. Glockling</i>	426
Introduction	426
Group III	427
Group IV	428
Group V	430
Vanadium, Niobium and Tantalum	430
Group VI	
Chromium, Molybdenum and Tungsten	430
Group VII	432
Manganese and Rhenium	432
Group VIII	433
Iron, Ruthenium and Osmium	433
Cobalt, Rhodium and Iridium	434
Nickel, Palladium and Platinum	434
Group Ib	446
Copper	446
Silver	447
Gold	449
Transition Metal Olefin-Complexes	451
Structure of Metal-Olefin Complexes	456
Acetylenic Derivatives of Transition Metals	458
Acetylene Derivatives of Type (a)	458
Acetylene Complexes of Type (b)	461
Acetylene Complexes of Type (c)	462

10. METAL CARBONYLS AND RELATED COMPOUNDS, <i>J. Chatt, P. L.</i>	
<i>Pauson and L. M. Venanzi</i>	468
Structure..	468
Considerations Governing the Constitution of Metal Carbonyls . .	468
Structures.	472
Nature of the Metal-Carbon and Carbon-Oxygen Bonds	474
Preparation.	480
Simple Carbonyls	480
The Polynuclear Carbonyls	482
Substitution Reactions in Metal Carbonyls	482
Displacement without Change in Oxidation State	483
Displacement with Disproportionation	491
Reactions with Acetylenes	492
The Carbonyl Hydrides and Related Compounds.	498
Introduction	498
Preparation of Carbonyl Hydrides	499
Properties.	499
Salts of the Hydrocarbonyls	503
Alkyl Metal Carbonyls	506
Metal Carbonyl Halides and Related Compounds	509
Preparation of the Noble Metal Derivatives.	511
The Manganese, Iron and Cobalt Carbonyl Halides.	512
Displacement Reactions of Carbonyl Halides.	513
Carbonyl Sulfides and Related Compounds.	513
Metal Nitrosocarbonyl and Nitrosoisonitrile Complexes	516
Cationic Isonitrile Complexes	517
AUTHOR INDEX	529
SUBJECT INDEX	545