

## Table of Contents

### A. Historical Introduction

(by O. J. Scherer and M. Regitz) . . . . . 1

### B. Bonding Properties of Low Coordinated Phosphorus Compounds

(by W. W. Schoeller) . . . . . 5

1.	Introduction . . . . .	5	5.5	Reactivity . . . . .	18
2.	Bonding in Higher Main Group Chemistry . . . . .	6	5.5.1	Carbenic Behaviour . . . . .	18
2.1	The Inert s-Pair Effect . . . . .	6	5.5.2	Electron Demand in Diels-Alder Reactions . . . . .	18
2.2	Hybridization, Nonhybridization . . . . .	7	5.5.3	Sulfur Addition to P(III) Double Bonds . . . . .	19
2.3	Sizes of Atoms and Orbitals . . . . .	7	6.	Phosphacumulenes . . . . .	20
2.4	Polarizability . . . . .	7	7.	Allylic Systems . . . . .	21
2.5	Stereochemical Activity of the "Inert" s-Orbital . . . . .	8	7.1	Phosphenium and Nitrenium Cations . . . . .	21
3.	$\pi$ -Bond Strengths between First and Second Long Period Elements . . . . .	10	7.2	2-Phosphaallylic Cations . . . . .	21
4.	Triple Bonds . . . . .	11	8.	Bis(ylene)phosphoranes . . . . .	22
4.1	Cyanide vs. Isocyanide Homologues . . . . .	11	8.1	Structural Aspects . . . . .	22
4.2	Bridging Phenomena . . . . .	12	8.2	Electrocyclic Ring Closure . . . . .	23
5.	Double Bonded Phosphorus . . . . .	12	9.	Metaphosphates . . . . .	24
5.1	General Considerations . . . . .	12	10.	Phosphoranes . . . . .	24
5.2	Ionization Potentials, Redox Potentials . . . . .	13	11.	Phosphaaromatic Systems . . . . .	25
5.3	Iminophosphines . . . . .	14	12.	$\pi$ -Bonding in Phosphinonitrene and Phosphinocarbene . . . . .	25
5.3.1	Phosphinonitrene Isomerization . . . . .	14	13.	Ring Strain in Cyclophosphines . . . . .	25
5.3.2	Structural Effects . . . . .	15	14.	Metal Complexation of Phosphorus $\pi$ -Bonds . . . . .	26
5.3.3	<i>cis/trans</i> -Isomerization at Nitrogen . . . . .	16	14.1	$\eta^1$ -versus $\eta^2$ -Complexation . . . . .	26
5.4	Diphosphenes . . . . .	16	14.2	Sandwich Formation . . . . .	26
5.4.1	Structural Effects . . . . .	16	15.	References . . . . .	27

### C. Phosphorus Compounds with Coordination Number 1 . . . . . 33

1.	Phosphinidenes . . . . .	33	1.1	<i>In Situ</i> Generated Phosphinidenes (by F. Mathey) . . . . .	33
$\sigma^1, \lambda^1$ -P	$-\ddot{\text{P}}:$		1.1.1	Introduction . . . . .	33
			1.1.2	Syntheses . . . . .	34

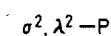
1.1.3	Reactions . . . . .	36	e)	Cyclopentadienes and Cyclohexa-			
1.1.4	Ligand Properties . . . . .	38		dienes . . . . .			82
1.1.4.1	General Remarks . . . . .	38	f)	1,3-Butadienes and Hetero-			
1.1.4.2	Synthesis of Terminal Phosphini-			1,3-dienes . . . . .			83
	dene Complexes . . . . .	38	2.4.2.5	Homo-Diels-Alder Reaction . . . . .			85
1.1.4.3	Reactions of Terminal Phosphini-		2.4.2.6	1,2-Addition . . . . .			86
	dene Complexes . . . . .	41		a) Halogen Compounds . . . . .			86
1.1.5	Addendum . . . . .	45		b) Organolithium Compounds . . . . .			87
1.2	Binuclear Phosphinidene			c) Enophiles . . . . .			87
	Compounds		2.4.3	Addendum . . . . .			89
	( <i>by G. Huttner and H. Lang</i> ) . . . . .	48	2.4.4	Acknowledgements . . . . .			89
1.2.1	Introduction . . . . .	48	2.5	The Behavior of $\sigma^1, \lambda^3$ -Phospha-			
1.2.2	Syntheses . . . . .	48		alkynes in the Coordination			
1.2.3	Bonding and Spectroscopy . . . . .	50		Sphere of a Transition Metal			
1.2.4	Reactivity . . . . .	53		( <i>by P. Binger</i> ) . . . . .			90
1.3	References . . . . .	55	2.5.1	Metal Complexes with			
				$\sigma^1, \lambda^3$ -Phosphaalkynes . . . . .			90
<b>2.</b>	<b>Phosphaalkynes (Alkylidyne-</b>		2.5.1.1	End-On Coordination . . . . .			90
	<b>phosphines)</b>		2.5.1.2	Side-On Coordination . . . . .			90
	( <i>by M. Regitz</i> ) . . . . .	58	2.5.2	Dimerization and Codimerization			
				of $\sigma^1, \lambda^3$ -Phosphaalkynes . . . . .			93
			2.5.2.1	Metal Complexes by Oxidative			
				Coupling of Two Phosphaalkynes . . . . .			94
			2.5.2.2	Metal Complexes by Oxidative			
				Coupling of One Phosphaalkyne			
				with Another Unsaturated System . . . . .			98
			2.5.3	Trimerization and Cotrimerization			
				of $\sigma^1, \lambda^3$ -Phosphaalkynes . . . . .			101
			2.5.3.1	Metal Complexes by Trimerization			
				of $\sigma^1, \lambda^3$ -Phosphaalkynes . . . . .			101
			2.5.3.2	Metal Complexes by Cotrimeri-			
				zation of $\sigma^1, \lambda^3$ -Phosphaalkynes			
				with Other Unsaturated Systems . . . . .			103
			2.5.4	Low-Coordinated Organic Phos-			
				phorus Compounds by Substitution			
				Reactions from Metal Complexes . . . . .			104
			2.5.5	Addendum . . . . .			105
			2.6	References . . . . .			107
			<b>3.</b>	<b>Phosphorus Nitride and Polyphos-</b>			
				<b>phorus Units</b>			
				( <i>by O. J. Scherer</i> ) . . . . .			112
			$\sigma^1, \lambda^3$ -P	:P $\equiv$ N:,	:P $\equiv$ P:,	P <sub>x</sub>	
2.1	General Remarks . . . . .	58	3.1	Introduction . . . . .			112
2.2	Physical Properties . . . . .	58	3.2	Syntheses . . . . .			112
2.3	Syntheses . . . . .	59	3.3	Ligand Properties . . . . .			112
2.3.1	Elimination Reactions . . . . .	59	3.3.1	The PN Unit as Ligand in Complexes . . . . .			112
2.3.1.1	Hydrogen Halide . . . . .	59	3.3.2	The P <sub>1</sub> Unit as Ligand in Complexes . . . . .			112
2.3.1.2	Chlorotrimethylsilane . . . . .	60	3.3.3	The P <sub>2</sub> Unit as Ligand in Complexes . . . . .			113
2.3.1.3	Hexamethyldisiloxane . . . . .	60	3.3.3.1	Complexes of the Tetrahedrane Type . . . . .			114
2.3.1.4	Lithium Trimethylsilanolate . . . . .	62	3.3.3.2	Complexes of the Butterfly Type . . . . .			114
2.3.2	Rearrangement Reactions . . . . .	62	3.3.3.3	<sup>31</sup> P-NMR and X-Ray Data . . . . .			114
2.3.3	Miscellaneous Syntheses . . . . .	63	3.3.4	The P <sub>3</sub> Unit as Ligand in Complexes . . . . .			117
2.4	Reactions . . . . .	64	3.3.4.1	Mononuclear Complexes with a			
2.4.1	Thermal Cyclooligomerizations:			Cyclo-P <sub>3</sub> Ligand . . . . .			117
	Tetraphosphacubane . . . . .	64	3.3.4.2	Reactivity of the Cyclo-P <sub>3</sub> Ligand . . . . .			117
2.4.2	Cycloaddition Reactions . . . . .	64					
2.4.2.1	[2+1]Cycloaddition . . . . .	64					
	a) Carbenes . . . . .	64					
	b) Silylenes and Germylenes . . . . .	67					
	c) Phosphinidenes . . . . .	67					
2.4.2.2	[2+2]Cycloaddition . . . . .	67					
2.4.2.3	[3+2]Cycloaddition . . . . .	68					
	a) Diazo Compounds . . . . .	68					
	b) Azides . . . . .	72					
	c) Nitrile Ylides . . . . .	73					
	d) Nitrile Imines . . . . .	74					
	e) Nitrile Oxides . . . . .	74					
	f) Nitrile Sulfides . . . . .	75					
	g) Mesoionic Compounds . . . . .	75					
	h) Nitrones and Azomethanimines . . . . .	76					
	i) Selenoxocarbenes . . . . .	77					
2.4.2.4	[4+2]Cycloaddition . . . . .	77					
	a) Cyclobutadienes . . . . .	77					
	b) Azetes . . . . .	79					
	c) 1,3- $\lambda^5$ -Diphosphetes . . . . .	80					
	d) Cyclopentadienones, Phosphole						
	Sulfides, and $\alpha$ -Pyrones . . . . .	80					

3.3.4.3	Dinuclear Complexes with Cyclo-P <sub>3</sub> Ligands . . . . .	119	3.3.6	The Cyclo-P <sub>5</sub> Unit as Ligand in Complexes . . . . .	122
3.3.4.4	<sup>31</sup> P-NMR and X-Ray Data . . . . .	119	3.3.7	The Cyclo-P <sub>6</sub> Unit as Ligand in Complexes . . . . .	124
3.3.5	The P <sub>4</sub> Unit as Ligand in Complexes . . . . .	119	3.4	Addendum . . . . .	126
3.3.5.1	Two P <sub>2</sub> Units . . . . .	122	3.5	References . . . . .	127

## D. Phosphorus Compounds with Coordination Number 2 . . . . . 129

### 1. Phosphonium Cations

(by M. Sanchez, M. R. Mazières, L. Lamandé, and R. Wolf) . . . . . 129



1.1	Introduction . . . . .	129
1.2	Syntheses . . . . .	130
1.2.1	From Halophosphines R <sub>2</sub> PX, RPX <sub>2</sub> . . . . .	130
1.2.1.1	Phosphorus-Halogen Bond Heterolysis . . . . .	130
1.2.1.2	Condensation Reactions with Trimethylsilyl Triflate . . . . .	131
1.2.2	Chlorophosphonium Cations . . . . .	131
1.2.3	From Iminophosphines R <sup>1</sup> -P=N-R <sup>2</sup> . . . . .	131
1.3	Physical Properties . . . . .	132
1.3.1	X-Ray Crystallography . . . . .	132
1.3.2	NMR Spectroscopy . . . . .	132
1.3.3	Theoretical Calculations . . . . .	133
1.4	Chemical Properties . . . . .	133
1.4.1	Lewis Acidity . . . . .	133
1.4.1.1	Reactions with Pyridine and Amines . . . . .	133
1.4.1.2	Reactions with Phosphines . . . . .	134
1.4.2	Insertion Reactions with C-H and C-C Bonds . . . . .	135
1.4.2.1	Oxidative Addition to a C-H Bond . . . . .	135
1.4.2.2	Insertion into a C-C Bond . . . . .	136
1.4.3	Reactions with Organic Species Possessing an X=N Bond (X=N, C, P) . . . . .	136
1.4.3.1	Reactions with Azides . . . . .	136
1.4.3.2	Reactions with Amidines and Isocyanides . . . . .	137
	a) Amidines . . . . .	137
	b) Isocyanides . . . . .	137
1.4.3.3	Reactions with Iminophosphines: R <sup>1</sup> -P=N-R <sup>2</sup> . . . . .	137
1.4.4	Cycloadditions with Dienes and Cyclooctatetraene . . . . .	138
1.4.4.1	1,3-Dienes . . . . .	138
1.4.4.2	1,4-Dienes . . . . .	139
1.4.4.3	Cycloocta-1,5-diene and Cyclooctatetraene . . . . .	139

1.4.5	Reactions with Alkynes . . . . .	139
1.5	Coordination Chemistry . . . . .	140
1.5.1	General Remarks . . . . .	140
1.5.1.1	Metallophosphonium Ions . . . . .	140
1.5.1.2	Phosphonium Ions as Ligands . . . . .	141
1.5.2	Metallophosphonium Species . . . . .	141
1.5.3	Phosphonium Cations as Two Electron Ligands . . . . .	142
1.5.3.1	Preparation by Ligand Substitution . . . . .	142
1.5.3.2	Preparation by Anionic Abstraction in Complexes . . . . .	143
1.5.4	Crystal Structures by X-Ray Diffraction and <sup>31</sup> P-NMR Spectroscopy . . . . .	144
1.5.5	Chemical Properties . . . . .	144
1.5.6	"Neutral Phosphonium Species" . . . . .	145
1.6	References . . . . .	146

### 2. 2-Phosphaallylic Cations

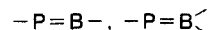
(by A. Schmidpeter) . . . . . 149



2.1	Introduction . . . . .	149
2.2	Syntheses . . . . .	150
2.3	Spectral Properties . . . . .	152
2.3.1	NMR Spectra . . . . .	152
2.3.2	UV/VIS Spectra . . . . .	152
2.4	Reactions . . . . .	152
2.5	Structures . . . . .	154
2.6	References . . . . .	154

### 3. Phosphinylideneboranes and Phosphinylideneborates

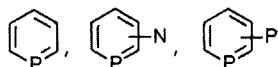
(by F. Bickelhaupt) . . . . . 155



3.1	Introduction . . . . .	155
3.2	Syntheses . . . . .	155
3.3	Structures . . . . .	156
3.4	Chemical Reactions . . . . .	156
3.5	References . . . . .	156

<b>4. Phosphaalkenes, Phospha-carbaoligoenes, and Phosphaallenes</b> (by R. Appel) . . . . .	157
$\sigma^2, \lambda^3 - P \quad -P=C \begin{array}{l} / \\ \backslash \end{array}, -P=C=X=Y, -P=P-X=Y,$ $-P=C=E$	
4.1 Introduction and Historical Aspects . . . . .	157
4.2 Formation of the P=C Double Bond . . . . .	158
4.2.1 By 1,2-Elimination . . . . .	158
4.2.2 By Condensation Reactions . . . . .	158
4.2.3 By 1,3-Trimethylsilyl Migration . . . . .	158
4.2.3.1 Condensation and Silatropy . . . . .	158
4.2.3.2 Addition and Silatropy . . . . .	158
4.2.4 By Carbene Addition . . . . .	159
4.3 Structures and Proof of Genuine $p\pi$ -Bonds . . . . .	160
4.4 Reactivity . . . . .	160
4.4.1 Reaction at the Phosphorus Atom . . . . .	160
4.4.2 Reaction at the P=C Double Bond . . . . .	161
4.4.2.1 Addition of Proton Active Reagents . . . . .	161
4.4.2.2 Cycloadditions . . . . .	161
a) [2+1]Cycloadditions . . . . .	161
b) [2+2]Cycloadditions . . . . .	162
c) [3+2]Cycloadditions . . . . .	162
d) [4+2]Cycloadditions . . . . .	163
e) [4+2]Cycloadditions of Heterodienes . . . . .	165
f) [8+2]Cycloaddition . . . . .	166
4.4.3 Reaction at Peripheral Substituents . . . . .	166
4.4.4 1,2-Eliminations: Synthesis of Phosphaalkynes . . . . .	167
4.5 Compounds with Several P=P (and C=C) Double Bonds . . . . .	168
4.5.1 Phosphabutadienes . . . . .	168
4.5.1.1 Monophosphabutadienes . . . . .	168
4.5.1.2 Diphosphabutadienes . . . . .	169
a) 1,3-Diphosphabutadienes . . . . .	169
b) 2,3-Diphosphabutadienes . . . . .	169
c) 1,4-Diphosphabutadienes . . . . .	169
4.5.1.3 Triphosphabutadienes . . . . .	170
4.5.2 Phosphapentadienes . . . . .	171
4.5.2.1 1,3,5-Triphosphapenta-1,4-Dienes . . . . .	171
4.5.2.2 2,3,4-Triphosphapenta-1,4-Dienes . . . . .	172
4.5.3 Phosphahexadienes and „Phospha-Cope“ Rearrangements . . . . .	172
4.5.3.1 1,3,4,6-Tetraphosphahexa-1,5-Dienes . . . . .	172
4.5.3.2 3,4-Diphosphahexa-1,5-Dienes . . . . .	175
a) Estimation of the P=C Bond Energy . . . . .	176
b) Ring Expansion to Cyclic Diphosphines by Cope Rearrangement . . . . .	176
c) Balance of Energy . . . . .	177
4.5.3.3 1,6-Diphosphahexa-1,5-Dienes by Cope Rearrangement from 3,4-Diphosphahexa-1,5-Dienes . . . . .	177
4.5.3.4 Valence Isomerization of 3,4-Diphospha-1,5-hexadiyne in to 3,4-Bis(phosphamethylene)-1-cyclobutene . . . . .	178
4.5.3.5 1,3-Diphosphahexa-1,5-Dienes . . . . .	179
4.5.3.6 Monophosphahexadienes . . . . .	179
a) Rearrangement of 3-Phosphahexa-1,5-Dienes to 1-Phosphahexa-1,5-Dienes . . . . .	179
4.6 Cumulated Bond Systems with Participation of the P=C Double Bond . . . . .	181
4.6.1 Diphosphaallenes . . . . .	181
4.6.1.1 1,3-Diphosphaallenes . . . . .	181
4.6.1.2 1-Phosphaallenes . . . . .	182
4.6.1.3 Reactivity of 1-Phosphaallenes . . . . .	184
4.6.2 1-Phosphabuta-1,2,3-trienes . . . . .	185
4.6.3 1,4-Diphosphabutatrienes . . . . .	186
4.6.4 1-Aza-3-Phosphaallenes (Monophospha-carbodiimides) . . . . .	186
4.6.4.1 Reactivity of 1-Aza-3-phosphaallenes . . . . .	186
4.6.5 Phosphaketenes . . . . .	188
4.6.5.1 Reactivity of Phosphaketenes . . . . .	189
4.6.6 Phosphathioketenes . . . . .	190
4.7 Coordination Chemistry of Phosphaalkenes, Phosphaallenes, and Phospha-carbaoligoenes . . . . .	191
4.7.1 Phosphaalkene Complexes . . . . .	191
4.7.2 Phosphaallene (Allyl) Complexes . . . . .	195
4.7.3 Complexes with Cumulated Double Bonds . . . . .	197
4.7.4 Phospha-carbaoligoene Complexes . . . . .	199
4.7.5 Metallaphosphaalkenes . . . . .	200
4.7.6 Phosphaalkenyl Complexes with Metal-Carbon Bonds . . . . .	202
4.7.7 Metallaphosphabutadiene Complexes . . . . .	203
4.7.7.1 1-Phospha-4-metallabutadiene . . . . .	203
4.7.7.2 1,3-Diphospha-4-Metallabutadiene Complexes . . . . .	203
4.7.8 1,4-Diphospha-5-metallapentadienes . . . . .	203
4.8 Compilations of Acyclic Phosphaalkenes . . . . .	204
4.8.1 <i>P</i> -H-, <i>P</i> -Alkyl-, or <i>P</i> -Aryl-Substituted Phosphaalkenes . . . . .	204
4.8.2 <i>P</i> -Heteroatom-Substituted Phosphaalkenes . . . . .	207
4.8.3 Monophosphabutadienes . . . . .	209
4.8.4 Monoazamonophosphabutadienes . . . . .	210
4.8.5 Diphosphabutadienes . . . . .	210
4.8.6 Triphosphabutadienes . . . . .	211
4.8.7 Phosphaalkenes with the Methylene Carbon in a Ring System . . . . .	211
4.8.8 Miscellaneous Phosphaalkene Systems . . . . .	211

4.8.9	Phosphacumulenes . . . . .	212	Dichloro-, Trichloro-, and Tetra-	
4.9	Concluding Remarks . . . . .	212	chloro-5-phenyl- $\lambda^3$ -phosphinines . . . . .	227
4.10	Addendum . . . . .	213	5.2.3.3 Thermolysis of 1,1-Diamino- and	
4.11	References . . . . .	214	1,1-Di(alkylthio)- $\lambda^3$ -phosphinines . . . . .	228
			5.2.4 By [4+2]Cycloadditions . . . . .	228
5.	$\lambda^3$ -Phosphinines, Aza- $\lambda^3$ -Phosphinines,		5.2.4.1 Of Phosphaalkenes and Phospha-	
	and $\lambda^3$ , $\lambda^3$ -Diphosphinines		alkynes with $\alpha$ -Pyrone . . . . .	228
	(by G. Märkl) . . . . .	220	a) Phosphaalkenes . . . . .	228
			b) Phosphaalkynes . . . . .	229
			5.2.4.2 Of Phosphaalkenes and Phospha-	
			alkynes with Cyclopentadienones . . . . .	229
			5.2.4.3 Of Phosphaalkenes with Other	
			1,3-Dienes . . . . .	230
			5.2.4.4 Of 1,3- $\lambda^3$ -Azaphosphinines with	
			Alkynes . . . . .	230
			a) Functionally Substituted Alkynes . . . . .	230
			b) Phosphino- and Silyl-Sub-	
			stituted Alkynes . . . . .	231
			5.2.4.5 Of 2 <i>H</i> -Phospholes with Alkynes . . . . .	231
			5.2.5 By Reaction of Carbene Complexes	
			with <i>tert</i> -Butylphosphaethyne . . . . .	232
			5.2.6 By Aromatizing Rearrangement	
			Reactions . . . . .	232
			5.3 Structural, Physical, and Spectral	
			Properties of $\lambda^3$ -Phosphinines . . . . .	232
			5.3.1 Structural Data . . . . .	232
			5.3.2 $^1\text{H-NMR}$ Data . . . . .	233
			5.3.3 $^{13}\text{C}\{-^1\text{H}\}$ -NMR Spectra . . . . .	234
			5.3.4 Photoelectron (PE) Spectra . . . . .	235
			5.3.5 Resonance Energies and Electronic	
			Structure . . . . .	235
			5.3.6 $^{31}\text{P}\{-^1\text{H}\}$ -NMR Spectra . . . . .	236
			5.3.7 UV Spectra . . . . .	237
			5.3.8 Mass Spectra . . . . .	238
			5.4 Chemistry of $\lambda^3$ -Phosphinines . . . . .	238
			5.4.1 Basic and Nucleophilic Character . . . . .	238
			5.4.2 Reaction with Nucleophiles . . . . .	239
			5.4.2.1 With RLi and RMgX: 1 <i>R</i> - $\lambda^4$ -Phos-	
			phiminyl Anions . . . . .	239
			5.4.2.2 With Diazoalkanes: Diphospha-	
			chiropteradienes . . . . .	240
			5.4.2.3 With Alkali Metals: $\lambda^3$ -Phos-	
			phinine Radical Anions, Dianions,	
			and Trianions . . . . .	240
			5.4.3 Reactions with Radicals: 1 <i>R</i> -Phos-	
			phiminyl Radicals as Intermediates . . . . .	241
			5.4.3.1 With Diarylmercury Compounds . . . . .	241
			5.4.3.2 With Chlorine or Bromine . . . . .	241
			5.4.4 Oxidative Addition of Protic	
			Nucleophiles (Alcohols, Amines) . . . . .	242
			5.4.4.1 With Mercury Acetate in the	
			Presence of an Alcohol . . . . .	242
			5.4.4.2 With Mercury Acetate and	
			Secondary Amines . . . . .	242
			5.4.4.3 One Electron Oxidation: $\lambda^3$ -Phos-	
			phiminyl Radical Cations? . . . . .	242
			5.4.4.4 Oxidation with Oxygen, Singlet	
			Oxygen, Hydrogen Peroxide, or	
			Nitric Acid . . . . .	242

 $\sigma^2, \lambda^3\text{-P}$ 

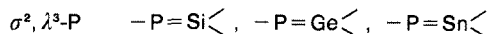
5.1	Introduction . . . . .	220
5.2	Syntheses of $\lambda^3$ -Phosphinines . . . . .	221
5.2.1	From Pyrylium Salts . . . . .	221
5.2.1.1	By O/P Exchange with	
	Tris(hydroxymethyl)phosphine . . . . .	221
5.2.1.2	By O/P Exchange with	
	Tris(trimethylsilyl)phosphine . . . . .	222
5.2.1.3	By O/P Exchange with $\text{PH}_3$ . . . . .	222
5.2.2	By Aromatization of 1,2- or	
	1,4-Dihydrophosphinines . . . . .	223
5.2.2.1	Dehydrohalogenation of 1-Halo-	
	1,4-dihydrophosphinines . . . . .	223
	a) Dehydrobromination of 1-Bromo-	
	1,4-dihydrophosphinines . . . . .	223
	b) Dehydrochlorination of <i>P</i> -Chloro-	
	benzo[ <i>c</i> ]-, -dibenzo[ <i>b,d</i> ]-, and	
	-dibenzo[ <i>b,e</i> ]dihydrophosphinines . . . . .	223
5.2.2.2	By Thermolysis of 1-Alkyl-1,2-	
	dihydrophosphinines . . . . .	224
	a) 2,4,6-Trisubstituted $\lambda^3$ -Phos-	
	phinines and 1-Phosphanaph-	
	thalene . . . . .	224
	b) 3,5-Di- and 3,4,5-Trisubstituted	
	$\lambda^3$ -Phosphinines from Phospha-	
	cyclohexenones . . . . .	224
	c) By Thermolysis of 1,2-Dihydro-	
	phosphinines Obtained by Ring	
	Enlargement of Phospholes . . . . .	225
5.2.2.3	By Thermolysis of 1,4-Dihydro-	
	phosphinines . . . . .	226
	a) Thermolysis of 1-Alkyl-1,4-	
	dihydrophosphinines . . . . .	226
	b) Thermolysis of 1-Bromo-4-	
	methoxy-4 <i>R</i> -1,4-dihydrophos-	
	phinines . . . . .	226
	c) From 4-Methoxy-4 <i>R</i> -1,4-di-	
	hydro-1 <i>H</i> -phosphinines . . . . .	227
5.2.3	By Thermolysis of $\lambda^5$ -Phosphinines . . . . .	227
5.2.3.1	Thermolysis of 1,1-Dialkyl- $\lambda^5$ -	
	phosphinines . . . . .	227
5.2.3.2	Thermolysis of 1- <i>tert</i> -Butyl-	
	1-chloro- $\lambda^5$ -phosphinines . . . . .	227
	a) 3 <i>R</i> - $\lambda^3$ -Phosphinines . . . . .	227
	b) 4-Methyl-3 <i>R</i> - $\lambda^3$ -phosphinines . . . . .	227
	c) 3-Chloro(bromo)-5-phenyl-	

5.4.5	Cycloaddition Reactions . . . . .	243	6.4	1,2,4-Diaza-, 1,2,4-Oxaza-, and 1,2,4-Thiazaphospholes . . . . .	263
5.4.5.1	$\lambda^3$ -Phosphinines as 1,3-Dienes . . . . .	243	6.4.1	Syntheses . . . . .	263
5.4.5.2	[4+2]Cycloadditions at the P=C Double Bond of $\lambda^3$ -Phosphinines as Dienophile . . . . .	244	6.4.2	Reactions . . . . .	264
5.4.5.3	[3+2]Cycloadditions at the P=C Double Bond of $\lambda^3$ -Phosphinines as Dipolarophile . . . . .	244	6.5	1,3,4-Diaza- and 1,3,4-Thiaza- phospholes . . . . .	265
5.4.5.4	[2+1]Cycloadditions at the P=C Double Bond of $\lambda^3$ -Phosphinines . . . . .	244	6.5.1	Syntheses . . . . .	265
	a) With Diazoalkanes as Carbene Precursors . . . . .	244	6.5.2	Reactions . . . . .	265
	b) With Halocarbenes . . . . .	245	6.6	1,2,3-Diazaphospholes . . . . .	267
5.4.6	Substitution Reactions . . . . .	246	6.6.1	Syntheses . . . . .	267
5.4.6.1	Electrophilic Substitution . . . . .	246	6.6.2	Reactions . . . . .	267
5.4.6.2	Substitution via $\lambda^5$ -Phosphinines . . . . .	246	6.6.2.1	<i>N</i> -Coordination and <i>N</i> -Substitution . . . . .	268
5.4.6.3	Substitution via 1 <i>R</i> -Phosphininyll Anions . . . . .	247	6.6.2.2	1,2-Addition and C4-Substitution . . . . .	268
5.4.6.4	Nucleophilic Substitution . . . . .	247	6.6.2.3	[4+2]- and [4+1]Cycloadditions . . . . .	269
5.5	Transition Metal Complexes of $\lambda^3$ -Phosphinines . . . . .	247	6.6.2.4	Dipolar [3+2]Cycloadditions . . . . .	269
5.5.1	$\sigma$ -Complexes . . . . .	247	6.6.2.5	Transition Metal Complexes . . . . .	271
5.5.2	$\pi$ -Complexes . . . . .	248	6.7	1,3,2-Diaza-, 1,3,2-Oxaza-, and 1,3,2-Thiazaphospholes . . . . .	271
5.5.3	$\sigma$ , $\pi$ -Complexes . . . . .	248	6.7.1	Syntheses . . . . .	271
5.5.4	Sandwich Complexes . . . . .	249	6.7.2	Reactions . . . . .	273
5.6	Aza- $\lambda^3$ -Phosphinines . . . . .	250	6.8	1,2,3,4-Triazaphospholes . . . . .	274
5.6.1	1,2- $\lambda^3$ -Azaphosphinines . . . . .	250	6.8.1	Syntheses . . . . .	274
5.6.2	1,4- $\lambda^3$ -Azaphosphinines . . . . .	250	6.8.2	Reactions . . . . .	274
5.6.3	1,3- $\lambda^3$ -Azaphosphinines . . . . .	250	6.9	1,2,4,3-Triazaphospholes . . . . .	275
5.7	$\lambda^3$ , $\lambda^3$ -Diphosphinines . . . . .	252	6.9.1	Syntheses . . . . .	275
5.7.1	1,3, 4,3-Diphosphinines . . . . .	252	6.9.2	Reactions . . . . .	276
5.7.2	Chemistry of the 1,3, 4,3-Diphos- phinine . . . . .	252	6.10	1,2,3-Aza-, 1,2,3,5-Diaza-, 1,2,4- Thia-, and 1,2,5-Thiadiphospholes . . . . .	279
5.8	Triphosphinines . . . . .	253	6.10.1	Syntheses . . . . .	279
5.8.1	2,4,6-Tris- <i>tert</i> -butyl-1,3,3,5,5- $\lambda^3$ - triphosphinine-molybdenum Complex . . . . .	254	6.10.2	Reactions . . . . .	279
5.8.2	1,2,3,5,5- $\lambda^3$ -Triphosphinine . . . . .	254	6.11	Spectra and Structure . . . . .	280
5.9	References . . . . .	254	6.11.1	UV/VIS Spectra . . . . .	280
			6.11.2	NMR Spectra . . . . .	280
			6.11.3	Structure Investigations . . . . .	281
			6.12	References . . . . .	283
<b>6.</b>	<b>Heterophospholes</b> (by <i>A. Schmidpeter and K. Karaghiosoff</i> )	258	<b>7.</b>	<b>Silylene-, Germylene-, and Stannylene phosphines</b> (by <i>F. Bickelhaupt</i> ) . . . . .	287

$\sigma^2, \lambda^3\text{-P}$



6.1	Introduction . . . . .	258
6.2	1,3-Aza-, 1,3-Oxa-, and 1,3-Thia- phospholes . . . . .	259
6.2.1	Syntheses . . . . .	259
6.2.2	Reactions . . . . .	261
6.3	1,2-Aza- and 1,2-Thiaphospholes . . . . .	262
6.3.1	Syntheses . . . . .	262
6.3.2	Reactions . . . . .	262

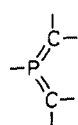
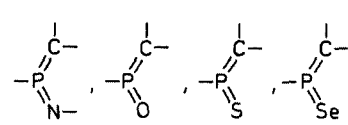


7.1	Silylenephosphines . . . . .	287
7.1.1	Syntheses . . . . .	287
7.1.2	Reactions . . . . .	288
7.1.3	Ligand Properties . . . . .	289
7.2	Germylene phosphines . . . . .	289
7.2.1	Syntheses . . . . .	289
7.2.2	Reactions . . . . .	290
7.2.3	Ligand Properties . . . . .	290
7.3	Stannylene phosphines . . . . .	290
7.3.1	Synthesis . . . . .	290
7.3.2	Reactions . . . . .	291
7.3.3	Ligand Properties . . . . .	292
7.4	Addendum . . . . .	292
7.5	References . . . . .	292

<b>8. Iminophosphines</b> (by <i>E. Niecke</i> ) . . . . .	293	<b>9. Phosphinylidene phosphines</b> (Diphosphenes) (by <i>M. Yoshifuji</i> ) . . . . .	321
$\sigma^2, \lambda^3\text{-P}$		$\sigma^2, \lambda^3\text{-P}$	
	$-\text{P}=\text{N}-$		$-\text{P}=\text{P}-$
8.1 Introduction . . . . .	293	9.1 Syntheses . . . . .	321
8.2 Syntheses . . . . .	293	9.1.1 Historical Background . . . . .	321
8.2.1 1,2-Elimination Reactions . . . . .	293	9.1.2 Preparative Methods . . . . .	322
8.2.2 Substitution Reactions . . . . .	294	9.2 Reactions . . . . .	326
8.2.3 Rearrangement Reactions . . . . .	295	9.2.1 Addition Reactions to the P=P	
8.2.4 Cycloreversion Reactions . . . . .	296	Double Bond . . . . .	326
8.2.5 1,1-Elimination Reactions . . . . .	296	9.2.1.1 With Electrophiles . . . . .	326
8.3 Structure and Bonding . . . . .	297	a) Oxidation . . . . .	326
8.3.1 Theoretical Studies . . . . .	297	b) Sulfurization . . . . .	327
8.3.2 Crystal Structures . . . . .	297	c) Halogenation . . . . .	327
8.3.3 Spectroscopic Properties . . . . .	300	d) Hydrolysis . . . . .	328
8.3.3.1 NMR Spectroscopy . . . . .	300	9.2.1.2 With Nucleophiles . . . . .	328
8.3.3.2 Photo-Electron and UV/VIS		a) Reduction . . . . .	328
Spectroscopy . . . . .	301	b) Organolithium Reagents . . . . .	329
8.3.3.3 Vibrational Spectroscopy . . . . .	302	9.2.1.3 With Radicals and Carbenes . . . . .	329
8.4 Reactivity of Iminophosphines . . . . .	302	9.2.1.4 Cycloadditions . . . . .	329
8.4.1 Addition Reactions . . . . .	302	9.2.2 Substitution Reactions . . . . .	330
8.4.1.1 With Lewis Bases . . . . .	302	9.2.3 Photoisomerization at the P=P	
8.4.1.2 With Lewis Acids . . . . .	303	Double Bond . . . . .	330
8.4.1.3 With Protic Reagents . . . . .	303	9.3 Ligand Properties . . . . .	331
8.4.1.4 Halometalation Reactions . . . . .	304	9.4 References . . . . .	336
8.4.1.5 Organometalation Reactions . . . . .	305		
8.4.1.6 Oxidative Addition Reactions . . . . .	305	<b>10. Phosphinylidene-<math>\sigma^4</math>-phosphoranes</b>	
8.4.2 Oligomerization Reactions . . . . .	306	<b>and Phosphinylidenesulfuranes</b>	
8.4.3 Cycloaddition Reactions . . . . .	308	(by <i>A. Schmidpeter</i> ) . . . . .	338
8.4.3.1 [2+1]Cycloadditions . . . . .	308		
8.4.3.2 [2+2]Cycloadditions . . . . .	309	$\sigma^2, \lambda^3\text{-P}$	$-\text{P}=\text{P}<$ , $-\text{P}=\text{S}<$
8.4.3.3 [2+3]Cycloadditions . . . . .	310	10.1 Introduction . . . . .	338
8.4.3.4 [4+1]Cycloadditions . . . . .	310	10.2 Phosphinylidene phosphinates/ Phosphinylphosphides . . . . .	338
8.4.4 Rearrangement Reactions . . . . .	310	10.2.1 Syntheses . . . . .	338
8.4.5 Reactions at Peripheral Substituents . . . . .	311	10.2.2 Reactions . . . . .	341
8.5 Coordination Compounds . . . . .	311	10.3 Neutral Phosphinylidene- $\sigma^4$ - phosphoranes and Phosphinyl- idenesulfuranes . . . . .	342
8.5.1 Iminophosphine Complexes . . . . .	311	10.3.1 Syntheses . . . . .	342
8.5.1.1 Iminophosphines as Two-Electron		10.3.2 Reactions . . . . .	344
Donors . . . . .	312	10.4 $1\sigma^2, 3\sigma^4$ -Triphosphenium Ions . . . . .	346
a) $\eta^1$ -(P)-Coordination . . . . .	312	10.4.1 Syntheses . . . . .	346
b) $\mu$ -(P)-Coordination . . . . .	313	10.4.2 Reactions . . . . .	346
c) $\eta^2$ -(PN)-Coordination . . . . .	313	10.5 Spectral Properties and Structures . . . . .	350
8.5.1.2 Iminophosphines as Four-Electron		10.5.1 $^{31}\text{P}$ -NMR Spectra . . . . .	350
Donors . . . . .	313	10.5.2 X-Ray Crystal Structures . . . . .	350
a) $\mu, \eta^1, \eta^1$ -(PN)-Coordination . . . . .	313	10.6 References . . . . .	351
b) $\mu_3, \eta^2$ -(PN)-Coordination . . . . .	314		
8.5.1.3 Iminophosphines as Six-Electron			
Donors . . . . .	314		
8.5.2 Metalloiminophosphines . . . . .	314		
8.5.3 Structure and Bonding in Imino- phosphine Coordination			
Compounds . . . . .	315		
8.6 Addendum . . . . .	317		
8.7 Acknowledgements . . . . .	317		
8.8 References . . . . .	317		

11.	<b>Oxo-, Thio-, and Selenoxophosphines</b> (by L. D. Quin and J. Szweczyk) . . . . .	352
	$\sigma^2, \lambda^3\text{-P}$ $\text{-P=O, -P=S, -P=Se}$	
11.1	Introduction . . . . .	352
11.2	Species Generated and Directly Observed by Spectral Techniques . . . . .	353
11.2.1	Halooxophosphines and Halothioxo- phosphines . . . . .	353
11.2.1.1	Generation Methods and Chemical Properties . . . . .	353
11.2.1.2	IR Spectroscopy . . . . .	354
11.2.1.3	Photoelectron Spectroscopy . . . . .	354
11.2.1.4	Mass Spectroscopy . . . . .	354
11.2.2	Phosphenous Acid ( $\text{HO-P=O}$ ) . . . . .	354
11.2.3	Oxophosphine (HPO) . . . . .	355
11.2.4	Oxophosphines Generated Directly in the Mass Spectrometer . . . . .	355
11.2.5	Sulfuranylidene phosphines . . . . .	355
11.3	Oxo- and Thioxophosphines Stabilized in the Coordination Sphere of Metals . . . . .	356
11.3.1	Generation Within the Coordi- nation Sphere . . . . .	356
11.3.2	Trapping of Thioxophosphines Generated in the Presence of Coordinating Agents . . . . .	357
11.4	Generation of Chalcogeno- phosphines in the Presence of Trapping Agents . . . . .	358
11.4.1	General Remarks . . . . .	358
11.4.2	Precursors of Chalcogenophos- phines . . . . .	359
11.4.2.1	Derivatives of the 7-Phospha- norbornene System . . . . .	359
11.4.2.2	Phospholene Oxides . . . . .	360
11.4.2.3	Phosphirane Oxides . . . . .	360
11.4.2.4	Phosphonic and Thiophosphonic Chlorides . . . . .	360
11.4.2.5	Alkyl Phosphinates . . . . .	362
11.4.2.6	Phenyldithioxophosphorane . . . . .	362
11.4.2.7	Phosphorus(III) Halides . . . . .	363
11.5	Oxo- and Thioxophosphines as Postulated Transient Intermediates . . . . .	363
11.6	References . . . . .	365

## E. Phosphorus Compounds with Coordination Number 3 . . . . . 367

1.	<b>Bis(methylene)phosphoranes</b> (by R. Appel) . . . . .	367
	$\sigma^3, \lambda^5\text{-P}$ 	
1.1	Syntheses . . . . .	367
1.2	Structure . . . . .	369
1.3	Properties and Reactivity . . . . .	370
1.4	References . . . . .	374
2.	<b>Methylene(imino, oxo, thio-, and selenoxo)phosphoranes</b> (by H. Heydt) . . . . .	375
	$\sigma^3, \lambda^5\text{-P}$ 	
2.1	Imino(methylene)phosphoranes . . . . .	375
2.1.1	General Remarks . . . . .	375
2.1.2	Syntheses . . . . .	375
2.1.2.1	From Methylene phosphines . . . . .	375
2.1.2.2	From Iminophosphines . . . . .	375
	a) By Cycloaddition with Diazo- alkanes . . . . .	375
	b) Via 4,5-Dihydro-1,2,3,4-triaza- phospholes . . . . .	376
	c) By Reaction with Chlorobis- (trimethylsilyl)methane . . . . .	376
2.1.2.3	From Azidophosphines . . . . .	376
2.1.2.4	From (Trimethylsilylmethyl)- phosphinous Acid(Trimethylsilyl)- amides . . . . .	377
2.1.3	Reactions . . . . .	377
2.1.3.1	Intramolecular Reactions . . . . .	377
	a) With 1,3-Migration of a Silyl Group . . . . .	377
	b) With Ring Closure . . . . .	378
2.1.3.2	Intermolecular Reactions . . . . .	378
	a) Via [2+2]Cycloaddition . . . . .	378
	b) Via [2+1]Cycloaddition . . . . .	380
	c) Via 1,2-Addition . . . . .	381
2.2	Methylene(oxo)phosphoranes . . . . .	381
2.2.1	General Remarks . . . . .	381
2.2.2	Syntheses . . . . .	381
2.2.2.1	From Methylene phosphines . . . . .	381
2.2.2.2	From Allyl(vinyl)phosphinates . . . . .	382
2.2.2.3	From Diazomethylphosphine Oxides . . . . .	382
2.2.3	Reactions . . . . .	382
2.2.3.1	Via 1,2-Addition . . . . .	382
2.2.3.2	Via Cycloaddition . . . . .	383



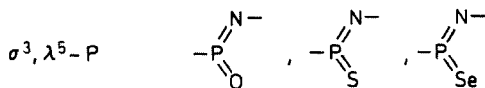
a) [2+2]Cycloaddition with Aldehydes . . . . .	383
b) [2+2]Cycloaddition with $\alpha, \beta$ -Unsaturated Carbonyl Compounds . . . . .	385
c) [4+2]Cycloaddition with $\alpha, \beta$ -Unsaturated Carbonyl Compounds . . . . .	385
d) [4+2]Cycloaddition with Aldehydes and Ketones . . . . .	385
e) Cycloaddition with Tropone or Tetraphenylcyclopentadienone . . . . .	386
2.3 Methylene(thio)phosphoranes . . . . .	386
2.3.1 General Remarks . . . . .	386
2.3.2 Syntheses . . . . .	386
2.3.2.1 From Methylenephosphines . . . . .	386
2.3.2.2 From Amino(thio)phosphines . . . . .	387
2.3.2.3 From Thiaphosphirane 2-Sulfides . . . . .	387
2.3.2.4 From 2-Phosphabicyclo[2.2.2]octa-5,7-diene 2-Sulfides . . . . .	388
2.3.2.5 From Allyl(vinyl)phosphine Sulfides . . . . .	388
2.3.2.6 From Thiophosphoryldiazo Compounds . . . . .	388
2.3.3 Reactions . . . . .	389
2.3.3.1 Via 1,2-Addition . . . . .	389
2.3.3.2 Via Cycloaddition . . . . .	389
a) [3+2]Cycloaddition . . . . .	389
b) [4+2]Cycloaddition . . . . .	390
2.4 Methylene(seleno)phosphoranes . . . . .	390
2.4.1 Syntheses and Reactions . . . . .	390
2.5 References . . . . .	390

### 3. Bis(imino)phosphoranes (by E. Niecke and D. Gudat) . . . . . 392



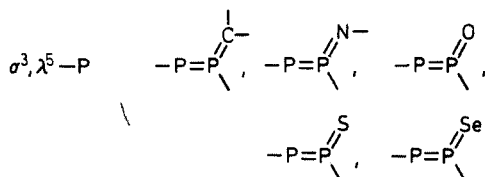
3.1 Introduction . . . . .	392
3.2 Syntheses . . . . .	392
3.3 Structure and Bonding . . . . .	394
3.3.1 Crystal Structures . . . . .	394
3.3.2 Theoretical and Physicochemical Studies . . . . .	396
3.4 Reactivity . . . . .	397
3.4.1 Addition Reactions . . . . .	397
3.4.1.1 Reactions with Protic Reagents . . . . .	397
3.4.1.2 Halo- and Organometalation Reactions . . . . .	398
3.4.2 Cycloaddition Reactions . . . . .	400
3.4.2.1 Oligomerization Reactions . . . . .	400
3.4.2.2 [2+2]Cycloadditions . . . . .	400
3.4.2.3 Other Cycloaddition Reactions . . . . .	402
3.5 Coordination Compounds . . . . .	402
3.6 References . . . . .	403

### 4. Imino-oxo-, Iminothio-, and Iminoselenoxophosphoranes (by E. Niecke and D. Gudat) . . . . . 405



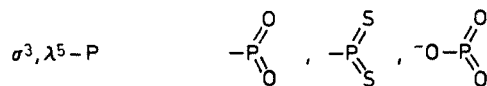
4.1 Introduction . . . . .	405
4.2 Synthesis, Structure, and Bonding . . . . .	405
4.3 Reactivity . . . . .	406
4.3.1 Addition Reactions . . . . .	406
4.3.2 Cycloaddition Reactions . . . . .	407
4.3.3 Ylide Transfer Reactions . . . . .	408
4.3.4 Coordination Chemistry . . . . .	408
4.4 References . . . . .	410

### 5. Phosphinylidene-methylene(imino, oxo, thio-, or seleno)phosphoranes (by M. Yoshifuji) . . . . . 411



5.1 Syntheses and Reactions . . . . .	411
5.1.1 Phosphinylidene(methylene)phosphoranes . . . . .	411
5.1.2 Phosphinylidene(imino)phosphoranes . . . . .	411
5.1.3 Phosphinylidene(oxo)phosphoranes . . . . .	411
5.1.4 Phosphinylidene(thio)phosphoranes . . . . .	412
5.1.5 Phosphinylidene(seleno)phosphoranes . . . . .	413
5.2 References . . . . .	414

### 6. Dioxo- and Dithioxophosphoranes including the Metaphosphate Anion (by M. Meisel) . . . . . 415



6.1 The Metaphosphate Ion . . . . .	415
6.1.1 Syntheses . . . . .	416
6.1.1.1 Hydrolysis of Phosphate Esters . . . . .	416
6.1.1.2 P-C Bond Cleavage of Phosphates . . . . .	418
a) Fragmentation of $\beta$ -Halophos-	

