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Transition and Main Group Metals in Cyclic Phosphazanes and Phosphazenes

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Contents

I. Abbreviations

Me	methyl
Et	ethyl
Pr	propyl
Bu	butyl
Ad	1-adamantyl
Ph	phenyl
Tol	tolyl
Cp	cyclopentadienyl
Cot	cyclooctatetraenediyl
Tmpip	2,2,6,6-tetramethylpiperidyl
OTf	trifluoromethylsulfonyl
Thf	tetrahydrofuran
Py	pyridine
Cod	η^2-1,5-cyclooctadiene
Bipy	2,2′-bipyridyl
Dppe	1,2-bis(diphenylphosphino)ethane
Dbu	diazabicycloundecene
lp	lone pair

II. Introduction

While the first nonphosphidic metal–phosphorus compound, $TiCl_4 \times PH_3$ was described by H. Rose[1] in 1832, the first metal–phosphorus–nitrogen compounds were synthesized in 1962, when D. S. Payne et al.[2] reported aminophosphane complexes of HgI_2 and CuI. The same group had also prepared the first cyclic compounds, diphosphazane chelates of Ni and Pd halides.[3] The earlier papers dealt mainly with coordination compounds, heterocycles containing covalent metal–phosphorus and metal–nitrogen bonds became available in the late 1970s, and the first cyclic compound with a metal–nitrogen multiple bond was described in 1986.[4]

The forthcoming interest in this field of inorganic chemistry is manifested in the increasing number of publications in the last 15 years due to different outstanding properties of these compounds making some of them useful candidates for catalytical and medical applications as well as precursors for new materials, e.g., polymers, semiconductors, etc.

The great variety of compounds is due to the different chemical behaviors of nitrogen and phosphorus sites. Nitrogen as a hard donor is capable of stabilizing metals in high oxidation states; the chelate effect may allow unusual coordination numbers and geometries as well. Phosphorus as a soft base is best suited to stabilize metals in low to medium oxidation states.

This article summarizes the field of cyclic metal–phosphorus–nitrogen systems; some facets of the material compiled here have been treated earlier under different aspects by different authors.[5–15] Main emphasis has been put upon compounds with covalent bonds from the metal to nitrogen or phosphorus; pure coordination compounds have been included if they have covalent counterparts or if complexation effects the stability of the resulting species. Literature coverage is maintained until early 1993.

III. Metal Bound to Phosphorus

Compounds with the metal bound to two phosphorus atoms can be roughly divided into two principal groups: (i) diphosphazane complexes where the P–N–P unit is attached to one metal atom yielding four-membered rings and complexes with the P–N–P core attached to two metal centers leading to eight-membered heterocycles (compounds with metal–metal bonds could also be considered to fall within the scope of this review, but since no covalent bonds from metal to phosphorus are present in these species they are excluded) and (ii) cyclodi- and tetraphosphazane complexes.

A. Diphosphazane Compounds

Three different bonding modes have been found with 1,2,4,3-azadiphosphametalletidines: (i) two covalent metal phosphorus bonds, (ii) one formally covalent and one dative bond resulting in zwitterionic species, and

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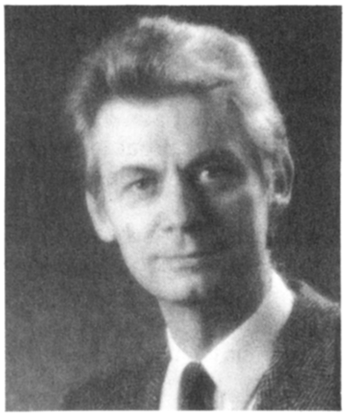
Michael Witt was born in 1952 in Frankfurt, Germany. He studied chemistry at the Johann-Wolfgang-Goethe-Universität in Frankfurt beginning in 1971 and graduated in 1976 with a Diplom degree and 1980 as Dr. phil. nat. in the research group of Prof. Dr. Dr. h.c. H. W. Roesky whom je joined in moving to the Georg-August-Universität in Göttingen (Germany) in 1980. From 1981 to 1982 he was a postdoctoral fellow in Prof. R. J. Lagow's group at the University of Texas at Austin. Afterward he again joined Prof. Roesky's group in Göttingen as a scientific teaching assistant. His current research interests are metal–nitrogen–phosphorus chemistry and problems of recycling and waste minimization.



Herbert W. Roesky was born in 1935 in Laukischken. He studied chemistry at the University of Göttingen, Germany, where he obtained his Diplom in 1961 and his Dr.rer.nat. in 1963. After one year of post-doctoral work at DuPoint in Wilmington, DE, he made his habilitation at University of Göttingen. In 1971 he became full professor in Frankfurt, and since 1980 he has been full professor and director of the Institute of Inorganic Chemistry at Göttingen University. During this time he has been visiting professor at Tokyo Institute of Technology and at Kyoto University in Japan. He is member of the Academy of Sciences in Göttingen and of the Academy of Scientists "Leopoldina" in Halle. He obtained many awards e.g. the Dr.rer.nat.h.c. of Bielefeld University, Alfred-Stock-Memorial Award, and French Alexander-von-Humboldt award. More than 550 research publications, articles, patents, and books document his activity.

(iii) chelate complexes where the phosphorus atoms act as donors only. These compounds are listed in Tables 1–3. Tables 4 and 5 contain bis- and trischelate complexes of type iii.

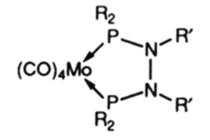
In the first three compounds of Table 2, **2a–c**, Li^+ serves as a counterion. Nickel compound **2e** consists of a chlorine-bridged dimer, the metals in spirocyclic complexes **2f** and **g** have square-planar environments in analogy to the corresponding diphosphanomethanide complexes.[21]

Most work in the field of diphosphazane chelates of type iii has been performed by the reesearch groups of J. Ellermann, W. Beck, D. S. Payne, and R. B. King. While the former three worked with tetraphenyldiphosphazanes, R. B. King and co-workers introduced tetrafluorodiphosphazane ligands to the metals. More than 100 of these complexes are known thus far. Since they only differ in R′ attached to nitrogen, they are comprised under one entry in Tables 3–5, unless X-ray structural information has been obtained. R′ most generally is H, Me, Et, Ph, PPh_2, or an alkylcarboxylate moiety $CHR''CO_2Me$. Complex ligands on the metal atom are summarized as L, and halides and pseudohalides as X.

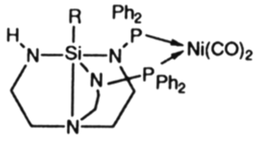
Group 6 complexes **4b–d** (Table 4) are cis-configurated. Reversible one-electron oxidation of **4b** (R′ = Me) yields a cationic trans complex.[60b]

Two different kinds of eight-membered ring systems are known, which can be considered as dimers of the formerly listed four-membered species, zwitterionic and chelate compounds, and they are listed in Tables 6 and 7, respectively. Compounds with metal–metal interactions (butterfly and "A-Frame" structures) are not tabulated.

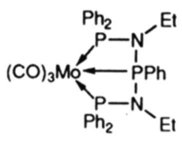
Aside from four- and eight-membered complexes, some five-membered hydrazine derivatives, **8**,[68,69] silicon-containing six-membered chelate complexes **9**,[70] and two different kinds of bicyclic η^3-chelates **10**[71] and **11**[72,73] with a phosphazane chain have been synthesized.



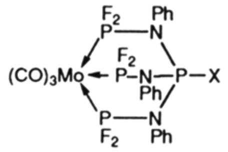
8a: R = Me, R′ = H
b: R = Me, R′ = Me
c: R = Me, R′ = $SiMe_3$
d: R = Ph, R′ = H
e: R = Ph, R′ = Me



9a: R = H
b: R = OEt



10



11a: X = lp
b: X = $Fe(CO)_4$

Compounds **10** and **11a** have been structurally characterized. Indications of complex formation of the ligand in **10** with Co^{2+} and Ni^{2+} have been mentioned, but no details are given.[74]

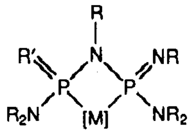
Six-membered chelate complexes with sulfur^{6+}, **12**, and sulfur^{4+}, **13**, have been reported (see Table 8).

The X-ray structures of **12b**, **13a**, and **13b** have been reported. While the change of oxidation states has only little effect on the S=N bond lengths, the P–N bonds in **13a,b** are slightly shorter than a calculated single bond,[77,78] and the P–N bonds in **12b** are significantly shorter, indicating multiple bonding.[75]

B. Cyclophosphazane Complexes

Only dimeric and tetrameric cyclophosphazane moieties have been found to act as chelating ligands, the cyclodiphosphazane in a η^2 fashion and the

Table 1. Four-Membered Heterocycles of Type i

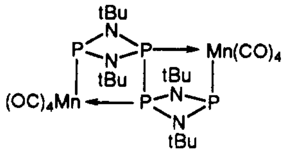


1

no.	[M]	R	R′	X-ray	ref(s)
1a	Ni(Bipy)	$SiMe_3$	lp	+	16,17
1b	Ni(Bipy)	$SiMe_3$	N-N=$CHCO_2$-tBu		17

cyclotetraphosphazanes in a η^3 fashion. They are listed in Tables 9 and 10.

Reductive coupling of cyclodiphosphazane moieties with P–Mn σ-bond formation occurs in the reaction of $NaMn(CO)_5$ with $(ClPN\text{-}tBu)_2$ to yield complex **15**. The X-ray structure shows two long and two short Mn–P bonds.[81b]

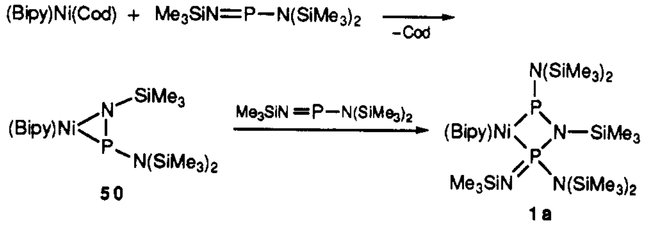


15f

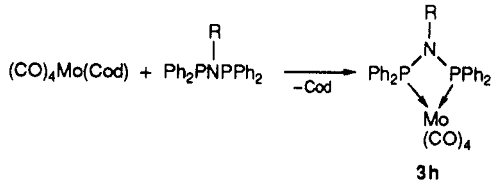
Compounds **16b,c,e** can be quaternized at the free phosphorus atom with the corresponding alkyl iodides to yield cationic complexes **16g–k**; treatment of **16j,k** with nBuLi affords ylidic complexes with insertion of CH_2 into the middle P–M bonds.[82]

C. Synthetic, Theoretical, and Structural Aspects

The syntheses of the diazaphosphametallidines **1–5** and tetraazadiphosphadimetallocines **6c** and **7** have been achieved by photochemical or thermal replacement of two monodentate or one labile bidentate ligand from the appropriate metal precursors, e.g.



(1)

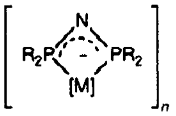


3h

(2)

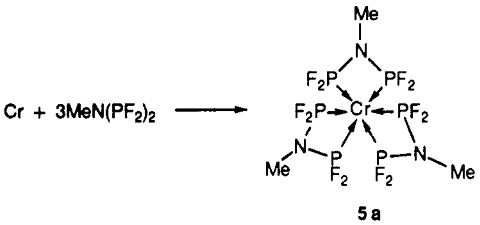
The other types of complexes described in this section, **8–16**, have been prepared in a similar way. While the first reaction sequence represents an oxidation of Ni in the first step and an oxidative [3 + 1] cycloaddition in the second step, the ligand exchange reactions proceed without change of oxidation states. Homoleptic bis(difluoro)diphosphazane complexes have been synthesized by cocondensation of metal vapor and the ligand at −190 °C, e.g. **5a**.

Table 2. Zwitterionic Four-Membered Heterocycles of Type ii



2

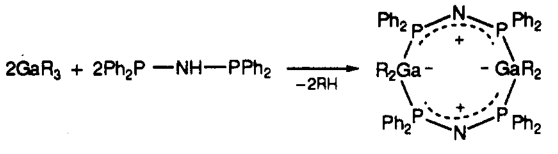
no.	[M]	R	*n*	ref(s)
2a	$Cr(CO)_4$	Ph	1	18,19
2b	$Mo(CO)_4$	Ph	1	19
2c	$W(CO)_4$	Ph	1	19
2d	$FeCp(CO)^+$	Ph	1	20
2e	$NiCl^+$	Ph	1	21
2f	Pd^{2+}	Ph	2	20,21
2g	Pt^{2+}	Ph	2	21



5a

(3)

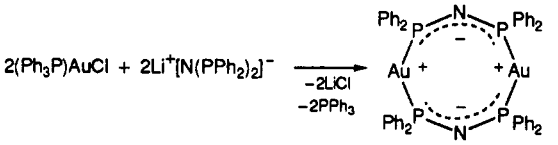
Zwitterionic **6a,b** are available by alkane elimination from GaR_3.



6a: R = Me
b: R = Et

(4)

While the electronic structure of **6a,b** is best described with gallanate anions and the positive charge delocalized over the P–N–P skeletons, the charge distribution is inverse in the case of **6c**.



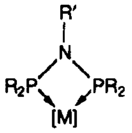
6c

(5)

The nitrogen atoms in **6c** can serve as donor sites for group 10 metal complexes to yield complexes **7k,l** (the X-ray structure of the latter has been reported).[64b]

X-ray structural analyses of several complexes **3**, **4**, **7**, **8**, **10**, and **11** have been performed. The P–N bonds of the ligands are in general a little shorter (1.67–1.69 pm) compared to 1.69 pm in $HN(PPh_2)_2$[85] and $PhN(PPh_2)_2$;[86] slightly longer bonds have been found in Pd complexes **3an** and **4y** (172.5 and 169.9 pm), respectively. The metal–phosphorus bond lengths are in the region found in other phosphane complexes. UV-photoelectron spectra of **5a,c,d** and **7h** have been reported,[87a] as well as Mössbauer spectra of **7i,j**.[87b] IR spectra of several **3m** compounds with different anions X have been discussed.[48c] The ^{31}P NMR shifts of most of the complexes are downfield of the uncomplexed ligands, the effect is decreasing in one group from the light to the heavier metals. While variation of the substituents on nitrogen causes no significant change in the $\Delta\delta$ values, e.g. **3e,p,v** (Me vs Et), it is strongly

Table 3. Diphosphazane Chelates of Type iii



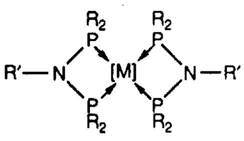
3

no.	[M]	R	R′	X-ray	ref(s)
3a	$VCp(CO)_2$	F	Me		22
3b	$Cr(CO)_4$	Ph	H, Me, iPr, CH_2CO_2Me, Ph, C(O)Ph, PPh_2, PPh_2AuCl, $AuPPh_3$		20,23–28d
	$[Cr(CO)_4$		$(\mu\text{-}AuPPh_2)_{1/2}]_2$		
3c	$Cr(CO)_3PPh_2NR'PPh_2$	Ph	H, Me		29
3d	$Cr(CO)_4$	OR″	Me, Ph		28b–d,30
3e	$Cr(CO)_4$	F	Me, Et, Ph		5,31,32a,b
3f	$Cr(CO)_4$	F	Ph		31,32
3g	$Cr(PF_2NMe_2)_4$	F	Me	+	33a,b,34
3h	$Mo(CO)_4$	Ph	H, Me, nPr, iPr, CH_2CO_2Me, CH-iPrCO_2Me, C_2H_4SMe, C(O)Ph, PPh_2, $AuPPh_3$ $AuPPh_3$		18,19,25–28b,35–37
3i	$Mo(CO)_4$	Ph	Et	+	35,36
3j	$Mo(CO)_3PR''_3$	Ph	H, CH_2CO_2Me		26,38
3k	$Mo(CO)_2Cp^+$	Ph	CH_2CO_2Me, $CHMeCO_2Me$, CH-iPrCO_2Me, CH_2Ph		39
3l	Mo(CO)(Cp)Cl	Ph	CH_2CO_2Me, $CHMeCO_2Me$, CH_2Ph		39
3m	$Mo(CO)_4$	NHPh	Ph	+	40a,b
3n	$Mo(CO)_4$	NR''_2	Ph		40a,b
3o	$Mo(CO)_4$	OR″	Me, Ph		28b,30
3p	$Mo(CO)_4$	F	Me, Et, Ph		5,31,32a,b
3q	$Mo(CO)_3(\eta^1\text{-}PF_2NMePF_2)$	F	Me		41
3r	$Mo(Cp)(Cl)(\eta^1\text{-}F_2PNMePF_2)$	F	Me	+	42
3s	$W(CO)_4$	Ph	H, CH_2CO_2Me, $CHMeCO_2Me$, PPh_2, $AuPPh_3$		19,26–28a
3t	$W(CO)_2Cp^+$	Ph	CH_2CO_2Me, CH-iPrCO_2Me		39
3u	W(CO)(Cp)Cl	Ph	CH_2CO_2Me, CH-iPrCO_2Me		39
3v	$W(CO)_4$	F	Me, Et, Ph		5,31,32a,b
3w	$Mn(CO)_3Br$	Ph	CH_2CO_2Me		26
3x	Mn(CO)Cp	F	Me		43
3y	$Mn(Cp)(\eta^1\text{-}PF_2NMePF_2)$	F	Me		43
3z	$Re(CO)_3NCO$	Ph	H	+	44a
3aa	$Fe(CO)_3$	F	Me		44b
3ab	$Fe(CO)Cp^+$	Ph	H, PPh_2		19,20
3ac	$Fe(\eta^1\text{-}PF_2NMePF_2)_3$	F	Me	+	33a,34,45
3ad	$Fe(PF_2NMe_2)_3$	F	Me		34
3ae	Co(CO)NO	Ph	H		25
3af	Rh(CO)Cl	Ph	CH-iPrCO_2Me		26,27
3ag	$Rh(Cod)^+$	OMe	Ph		46
3ah	$Rh(Dppe)L^+$	OMe	Me		46
3ai	$Ir(PPh_3)_2^+$	OMe	Me		46
3aj	$Ir(PPh_3)_2CO^+$	OMe	Me	+	46
3ak	$NiCp^+$	Ph	Me, Ph		47
3al	$Ni(PF_2NMe_2)_2$	F	Me		33
3am	NiX_2	Ph	Et, Ph		2,48a–c
3an	$PdCl_2$	Ph	Et	+	3,36,49
3ao	$PdCl_2$ [	Ph	iPr, CH_2CO_2Me, CH-iPrCO_2Me, $(\mu\text{-}C_2H_4\text{-}CHCO_2Me)_{1/2}]_2$		26,27,50a,b
3ap	$Pd(C_6X_5)_2$, X = F, Cl	Ph	H		65
3aq	$PtCl_2$ [	Ph	iPr, CH_2CO_2Me, CH-iPrCO_2Me, $(\mu\text{-}C_2H_4\text{-}CHCO_2Me)_{1/2}]_2$		26,27,50a,b
3ar	$Pt(C_6F_5)_2$	Ph	H		65
3as	$Cu(CN)PPh_3$	Ph	H	+	51
3at	$Cu(PPh_3)_2^+$	Ph	H	+	51,52
3au	$Mo(CO)_4$	Ph, NH-iPr	iPr	+	53a
3av	$Mo(CO)_4$	OPh	Ph	+	28b–d
3aw	$Mo(CO)_4$	Cl	Ph		40b
3ax	$Mo(CO)_3I_2$	Ph	iPr		28b,50b
3ay	$Mo(CO)_3I_2$	OPh	Me, Ph		28b,50b,53b
3az	$Mo(CO)_3Cl(SnCl_3)$	Ph	iPr		50b
3ba	$W(CO)_4$	Ph	iPr	+	28b–d
3bb	$W(CO)_4$	OR″	Me, Ph		28b–d
3bc	$W(CO)_3I_2$	Ph	iPr		28d,53c
3bd	$W(CO)_3I_2$	OPh	Me		28b,d,50b,53b
3be	$W(CO)_3I_2$	OPh	Ph	+	28d,50b,53b
3bf	$W(CO)_3Cl(SnCl_3)$	Ph	iPr		50b
3bg	$Fe(CO)_3$	Ph	Et	+	53c
3bh	$Fe(CO)_3$	Ph	iPr		28b–d
3bi	$Fe(CO)_3$	OPh	Me, Ph		28b–d
3bj	$Ru(CO)_3$	Ph	Et		53d

Table 3 (Continued)

no.	[M]	R	R′	X-ray	ref(s)
3bk	$Rh(\mu\text{-}Cl_2RhCot)$	OPh	Ph		28b,50b
3bl	$[Rh\mu\text{-}Cl$	OPh	Ph]$_2$		28b,50b
3bm	$PdCl_2$	OPh	Me, Ph		50b
3bn	PdR''_2, R″ = Me, Et, iPr	OPh	Ph		50b
3bo	$Pd(\eta^2\text{-}L)$	Ph	H		53e
3bp	$PtCl_2$	OPh	Me, Ph		50b

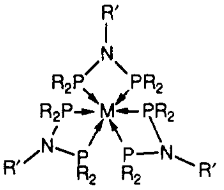
Table 4. Spirocyclic Bischelates



4

no.	[M]	R	R′	X-ray	ref(s)
4a	VCp	F	Me		22
4b	$Cr(CO)_2$	Ph	H, Me		25,29
4c	$Mo(CO)_2$	Ph	H		25
4d	$W(CO)_2$	Ph	H		19
4e	Fe(CO)	F	Me		54
4f	$Fe(\eta^1\text{-}PF_2NMePF_2)$	F	Me		33a
4g	Rh^+	Ph	H, Me, Et, Ph, pTol, CH_2CO_2Me, $CHMeCO_2Me$, CH-iPrCO_2Me		26,27,55–57
4h	$Rh(CO)^+$	Ph	H, Me, Et, Ph, pTol		55,56
4i	RhCl	Ph	Me, Et, Ph, pTol		56
4j	$Rh(\eta^2\text{-}O_2)^+$	Ph	H	+	55
4k	$Rh\eta^2\text{-}L^+$	Ph	H		55
4l	Rh^+	OMe	Ph		46
4m	$[Rh^+(\mu\text{-}(PR_2)_2NR')_{1/2}$	OMe	Ph]$_2$		46
4n	Ir^+	Ph	H, Me, Ph, pTol		58,59
4o	$IrCO^+$	Ph	H, Me, Ph, pTol		59
4p	IrH_2^+, cis/trans	Ph	pTol		60a
4q	$Ir(H)Cl^+$, trans	Ph	pTol		60a
4r	IrX_2^+	Ph	H		58
4s	$Ir(\eta^2\text{-}L)$	Ph	H		58
4t	$Ir(\eta^1\text{-}PhN(PR_2)_2)^+$	OMe	Me		46
4u	$IrPPh_3^+$	OMe	Me		40a
4v	Ni^{2+}	Ph	Ph		48a
4w	NiX^+	Ph	Ph		42
4x	Pd^{2+}	Ph	H		21
4y	Pd^{2+}	Ph	Me	+	21
4z	Pt^{2+}	Ph	H, Me		21,58
4aa	$Mo[\eta^1\text{-}(PR_2)_2NR']_2$	Ph	iPr		28b

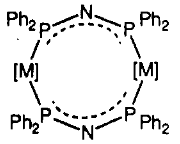
Table 5. Trischelates



5

no.	M	R	R′	ref(s)
5a	Cr	F	Me	32a,54
5b	Cr	F	Ph	61,62
5c	Mo	F	Me	54
5d	Mo	F	Ph	61,62
5e	W	F	Me	54
5f	W	F	Ph	61,62

Table 6. Zwitterionic Diazatetraphosphadimetallocines



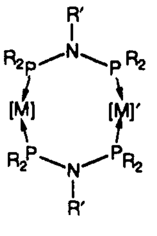
6

no.	[M]	ref(s)
6a	$GaMe_2$	63
6b	$GaEt_2$	63
6c	Au	20,64a,b

dependent on the substituents at the metal atoms, e.g. **3s** vs **4d** or **4n,o,s**. High-field shifts have been observed in bis(difluoro)diphosphazane complexes **3e,v** and **5e**, and in some cationic group 9 and 10 compounds. Selected ^{31}P NMR values are listed in Table 11.

In some compounds 4 several ^{31}P signals are found due to distorted geometries or nonequivalence of the phosphorus atoms. While protonation of **2f,g** to yield **4x,z** has only little effect on the chemical shift,[21] exchange of BPh_4^- for Cl^- in **4n** causes a high-field shift of 20 ppm, probably due to a geometrical change at the metal atom.[58] In other ionic compounds the difference found is within the range of 1–3 ppm. A drastic high-field shift of more than 200 ppm has been found in the cyclodiphosphazane complexes 14 and 15: δ $(ClPN\text{-}tBu)_2$ 207.7 ppm, $(ClPN\text{-}tBu)_2Fe(CO)_3$, **14a**–10.5 ppm.[79]

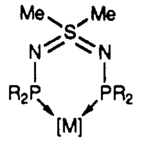
Table 7. Eight-Membered Chelate Complexes



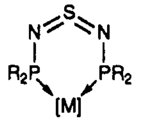
7

no.	[M]	[M]′	R	R′	X-ray	ref(s)
7a	$Fe(CO)_3$	[M]	F	Me		54
7b	$Fe(NO)_2$	[M]	Ph	H		25
7c	$Rh^+[\eta^2\text{-}(PR_2)_2NMe]$	[M]	OMe	Me	+	46
7d	Rh(CO)Cl (X = Cl, F)	[M]	OPh	Ph		28b
7e	$Pd(C_6F_5)_2$	Ag^+	Ph	H		65
7f	$Pt(C_6F_5)_2$	Ag^+	Ph	H		65
7g	$Ni[\eta^1\text{-}[(F_2P)_2NMe]_2]$	[M]	F	Me		54
7h	$Ni[\eta^2\text{-}(F_2P)_2NMe]$	[M]	F	Me		54
7i	AuCl	[M]	Ph	H, Me		20,66
7j	Au^+	[M]	Ph	H		20,67
7k	Au^+	[M]	Ph	AuC_6F_5		64b
7l	Au^+	[M]	Ph	$Ag(PPh_3)OClO_3$	+	64b

Table 8. Sulfur-Containing Chelates



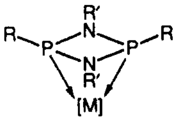
12



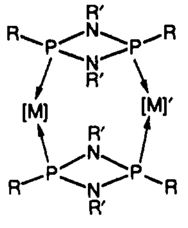
13

no.	[M]	R	X-ray	ref(s)
12a	$Cr(CO)_4$	Ph		75
12b	$Mo(CO)_4$	Ph	+	75
12c	$W(CO)_4$	Ph		75
13a	$Cr(CO)_4$	tBu	+	76
13b	$Cr(CO)_4$	Ph	+	77,78
13c	$Mo(CO)_4$	tBu		76
13d	$Mo(CO)_4$	Ph		77,78
13e	$W(CO)_4$	tBu		76

Table 9. Cyclodiphosphazane Complexes



14



15

no.	[M]	[M]′	R	R′	X-ray	ref
14a	$TiCl_4$		Cl	tBu		79
14b	$Fe(CO)_3$		Cl	tBu		79
14c	$NiCp^+$		Cl	tBu		80
15a	$Mo(CO)_4$	[M]	O-pTol	Ph	+	81a
15b	$Mo(CO)_4$	$PtCl_2$	O-pTol	Ph		81a
15c	Rh(CO)Cl	[M]	Cl	tBu		79
15d	Rh(CO)Cl	[M]	OPh	tBu		50b
15e	$PdCl_2$	[M]	$[\mu\text{-}(OCH_2)_2]_{1/2}$	Ph		28d

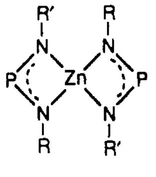
IV. Metal Bound to Nitrogen

A subdivision has been made concerning the bond order around the metal atoms, section A deals with compounds with bond orders ≤ 1 involving coordinative bonding and section B, with metallacyclophosphazenes with conjugated electron systems.

A. Compounds with Coordinative and Single Bonds to the Metal

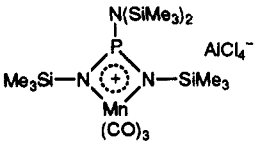
The majority of compounds in this section contain a four-membered MN_2P ring. Compounds **17** with trivalent (Table 12) and **18** with pentavalent phosphorus (Table 13) are known as well as metallaspiroheptanes **19** (Table 14). Probable resonance structures of these heterocycles are discussed in section III.C.

Starting from $Zn[N(SiMe_3)_2]_2$ and dimeric aminoiminophosphanes, spirocyclic λ^3-compounds **17l-n** are available with elimination of hexamethyldisilazane. The X-ray structure of **17n** shows zinc to have a tetrahedral environment.[95c]

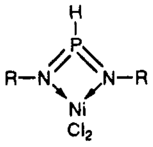


17l: R = R′ = tBu
m: R = Ad; R′ = 2,6-$(iPr)_2C_6H_3$
n: R = R′ = 2,4,6-$(tBu)_3C_6H_2$

In addition, one cationic complex **20**,[127] available by chloride abstraction with $AlCl_3$ from **18av**, and a λ^5-diiminophosphorane complex **21**, which on the basis of spectroscopical data has the depicted formula,[90] have been synthesized.



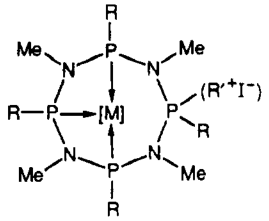
20



21: R = 2,4,6-$(tBu)_3C_6H_2$

Eight-membered dimeric alkali aminoiminophosphinates **22** have been postulated earlier from molecular weight determinations,[98,107a,128] but seem to be rather

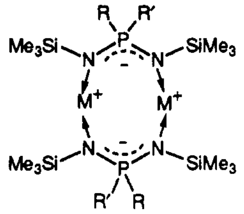
Table 10. Cyclotetraphosphazane Complexes



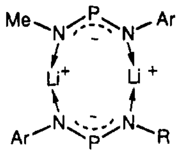
16

no.	[M]	R	$(R')^+$	X-ray	ref(s)
16a	$Mn(CO)_3^+$	Me			82
16b	$Cr(CO)_3$	Me			82
16c	$Mo(CO)_3$	Me		+	82,83
16d	$Mo(CO)_3$	Et			82
16e	$W(CO)_3$	Me			82
16f	$CoCl^+$	Me			82
16g	$Cr(CO)_3$	Me	Me		82
16h	$Cr(CO)_3$	Me	CH_2CN		82
16i	$Cr(CO)_3$	Me	$CH_2C(O)NH_2$		82
16j	$Mo(CO)_3$	Me	Me	+	82,84
16k	$W(CO)_3$	Me	Me		82

unlikely in the light of new X-ray structural determinations of **18a** and **19a**,[96,97] but this structural feature has been found in the trivalent compounds **22e**,**d**, while the bulkier CPh_3 group results in the formation of the four-membered ring **17k**.[95b]



22a: M = Li, R = tBu, R′ = NMe_2
b: M = Na, R = R′ = Ph



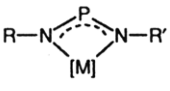
22c: R = tBu, Ar = 2,4,6-$(tBu)_3C_6H_2$
d: R = Ad, Ar = 2,4,6-$(tBu)_3C_6H_2$

A silicon-bridged eight-membered ring **23** has been synthesized, and its structure has been derived from NMR spectroscopical data.[129]

Table 11. Selected ^{31}P NMR Shifts

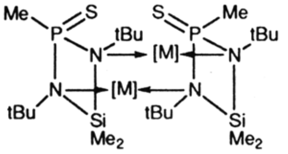
no.	compound	δ (ppm)	Δδ (ppm)	ref(s)
	$HN(PPh_2)_2 \hat{=} L^1$	42.7		25
3b	$Cr(CO)_4L^1$	96	+53.3	25
3h	$Mo(CO)_4L^1$	70	+27.3	28a
3s	$W(CO)_4L^1$	42.8	+0.1	28a
3ab	$Fe^+(CO)(Cp)L^1$	~90	~+47	20
3at	$Cu^+(PPh_3)_2L^1$	51	+8.3	52
4b	$Cr(CO)_2(L^1)_2$	109.7, 90	+67, +47.3	25
4c	$Mo(CO)_2(L^1)_2$	84.8, 64.3	+42.1, +21.6	25
4d	$W(CO)_2(L^1)_2$	56.1	+13.4	19
4g	$Rh^+(L^1)_2$	~44	+1	55
4h	$Rh^+(CO)(L^1)_2$	~37	−6	55
4n	$Ir^+(L^1)_2Cl^-$	29.5	−12.8	58
4n	$Ir^+(L^1)_2BPh_4^-$	9.2	−33.5	58
4o	$Ir^+(CO)(L^1)_2$	0.4	−42.3	58
4s	$Ir^+\eta^2\text{-}(O_2)(L^1)_2$	−10, −15.4	−52.3, −58.1	58
4x	$Pd^{2+}(L^1)_2$	29.6	−13.1	21
4z	$Pt^{2+}(L^1)_2$	23.0	−19.7	21
7b	$(Fe(NO)_2L^1)_2$	98.5	+55.8	25
3ap	$Pd(C_6F_5)_2L^1$	28.7	−14	65
7e	$[Pd(C_6F_5)_2(L^1)_2Ag^+]$	59.7 (Pd), 61.2 (Ag)	+17, +18.5	65
3ar	$Pt(C_6F_5)_2L^1$	17.1	−25.6	65
7f	$[Pt(C_6F_5)_2(L^1)_2Ag^+]$	47.4 (Pt), 56.2 (Ag)	+4.7, +13.5	65
7j	$(Au^+L^1)_2$	~79	~+36	20
	$LiN(PPh_2)_2 \hat{=} LiL^2$	41.2		88
2d	$Fe(CO)(Cp)L^2$	45.4	+4.2	20
2e	$(NiClL^2)_2$	57	+15.8	21
2f	$Pd(L^2)_2$	25.5	−15.7	21
2g	$Pt(L^2)_2$	25.0	−16.2	21
6a	$(GaMe_2L^2)_2$	41.8	+0.6	63
6b	$(GaEt_2L^2)_2$	66	+24.8	63
6c	$(AuL^2)_2$	53.3	+12.1	20
	$EtN(PF_2)_2 \hat{=} L^3$	145.3		89
3e	$Cr(CO)_4L^3$	170.7	+25.4	32b
3p	$Mo(CO)_4L^3$	144.8	−0.5	32b
3v	$W(CO)_4L^3$	114.0	−31.3	32b
	$MeN(PF_2)_2 \hat{=} L^4$	141.5		32a,89
3e	$Cr(CO)_4L^4$	168.5	+27	32a
3p	$Mo(CO)_4L^4$	144.5	+3	32a
3v	$W(CO)_4L^4$	112.4	−29.1	32a
5a	$Cr(L^4)_3$	180.3	+38.8	54
5c	$Mo(L^4)_3$	157.3	+15.8	54
5e	$W(L^4)_3$	125.2	−16.3	54
	$PhN[P(OMe)_2]_2 \hat{=} L^5$	142.5		46
3ag	$Rh^+(Cod)L^5$	103.7	−38.8	46
4e	$Rh^+(L^5)_2$	121.2	−21.3	46

Table 12. 1,3,2λ^3,4-Diazaphosphametalletidines



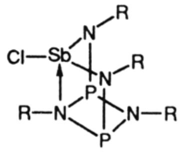
17

no.	[M]	R	R′	X-ray	ref(s)
17a	Li	2,4,6-$(tBu)_3C_6H_2$	R		90
17b	$AlMe_2$	2,4,6-$(tBu)_3C_6H_2$	R	+	90
17C	$AlCl_2$	$SiMe_3$	R		91–94
17d	$AlCl_2$	tBu	$SiMe_3$	+	91
17e	$AlBr_2$	$SiMe_3$	R		91
17f	AlI_2	$SiMe_3$	R		91
17g	$SnMe_3$	tBu	R		95a
17h	$SnMe_2Bu$	tBu	R		95a
17i	$SnMe_2Ph$	tBu	R		95a
17j	$SnMe_2Cl$	tBu	R		95a
17k	$Li(OEt_2)$	2,4,6-$(tBu)_3C_6H_2$	CPh_3	+	95b

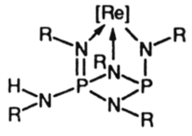


23: [M] = $Re(CO)_3Br$

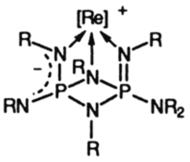
Several cage compounds of Sb, **24**,[130] and Re ([Re] = $Re(CO)_3$), **25a**,[117] **25b**,[115,131] **26**,[118] and **27**,[118] are known, which contain four-membered MN_2P rings (R = $SiMe_3$).



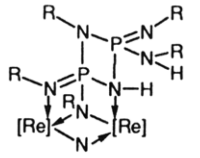
24



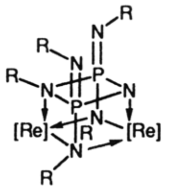
25a



25b



26

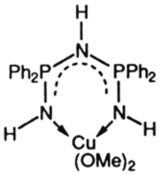


27

The first four compounds have been characterized by X-ray structure analyses, and the structure of **27** is consistent with its NMR spectra.

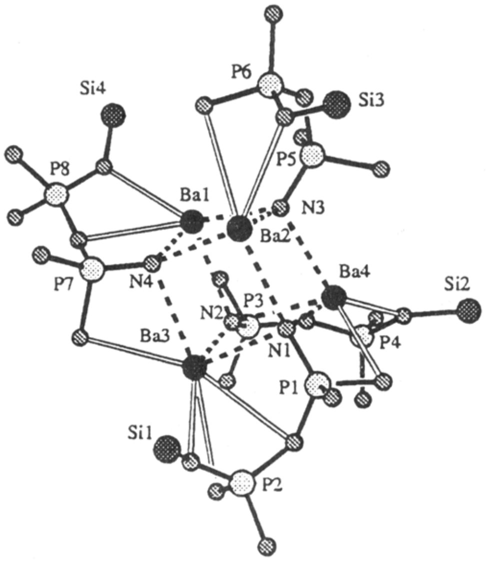
A clear distinction concerning the charge distribution can be made between 1,5-η^2 bound zwitterionic chelates **28** with a cationic N_3P_2 backbone (Table 15) and anionic 1,5-η^2 and 1,3,5-η^3 complexes **29** (Table 16). In compounds that have not been structurally characterized the hapticity stays uncertain, the only true anionic η^2-complex is dimeric Li salt **29l** with a centrosymmetric Li_2N_2 core.[136]

A neutral chelate complex of Cu, **30**, is also known.[140]



30

In addition to **29j**, the reaction of $Ba[N(SiMe_3)_2]_2$ with the phosphazene precursor leads to an interesting cluster with four Ba atoms, **31**, where all metal atoms have significantly different environments.[138]



31 $\{Ba[NP(NMe_2)_2]_2NSiMe_3\}_4$
(methyl groups omitted)

A series of cyclophosphazene complexes **32** has been reported. Although six-membered cyclophosphazenes represent the majority of known compounds, only one complex **32a**[141] has been synthesized thus far. It was first believed that it was a π-complex, but subsequent X-ray studies showed the metals to be coordinated through nitrogen only. Table 17 lists the complexes **32** known so far. In addition, poorly characterized $CoCl_2$ and NiX_2 complexes with two metal centers on one cyclononaphosphazene have been mentioned.[142]

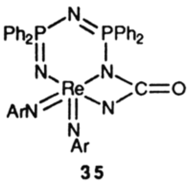
Another bonding mode, η^2-exocyclic/endocyclic has been found in some amino-substituted cyclophosphazenes **33** (Table 18).

In addition to **32** and **33**, various $M(CO)_3$ and $M(CO)_4$ complexes of cyclophosphazenes with cyclic amino substituents have been reported, but no structural assignment has been made.[157]

B. Heterocycles with Metal–Nitrogen Multiple Bonds

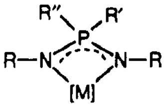
The compounds summarized in this section can be considered as derivatives of cyclophosphazenes of different ring sizes, where one or two metal fragments replace PR_2 units. As in phosphazene chemistry six-membered triazadiphosphametallines **34** represent the greatest group of these compounds; they are listed in Table 19.

A compound **35**, a formal [2 + 2] addition product of ArN=C=O (Ar = 2,6-$iPr_2C_6H_3$) to an unknown precursor **34y**, [M] = $Re(NAr)_2$ has been synthesized from **34v** and ArN=C=O. Its structure has been proved by X-ray analysis and mass and multinuclear NMR spectroscopy.[166]



35

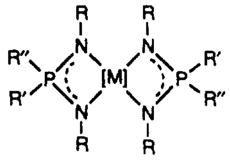
Table 13. 1,3,2λ^5,4-Diazaphosphametalletidines



18

no.	[M]	R	R′	R″	X-ray	ref(s)
18a	Li(Thf)$_2$	SiMe$_3$	Ph	Ph	+	96,97
18b	K(Thf)$_4$	SiMe$_3$	Ph	Ph	+	97
18c	[Rb(Thf)	SiMe$_3$	Ph	Ph]$_2$	+	97
18d	[(Cs	SiMe$_3$	Ph	Ph)$_2$]$_\infty$	+	97
18e	AlMe$_2$	SiMe$_3$	H	N(SiMe$_3$)$_2$		98
18f	AlMe$_2$	tBu	Me	SiMe$_3$		99
18g	AlMe$_2$	SiMe$_3$	Me	SiMe$_3$		99
18h	AlMe$_2$	tBu	Me	N-tBu(SiMe$_3$)		98,100,101
18i	AlMe$_2$	SiMe$_3$	Me	Tmpip		98,100
18j	AlMe$_2$	SiMe$_3$	Me	N(SiMe$_3$)$_2$		98,100
18k	AlMe$_2$	SiMe$_3$	Ph	Ph		102
18l	AlMeCl	SiMe$_3$	Me	N(SiMe$_3$)$_2$		98
18m	AlPh$_2$	SiMe$_3$	Ph	N(SiMe$_3$)$_2$	+	98,103
18n	AlCl$_2$	SiMe$_3$	Me	N(SiMe$_3$)$_2$		98,104
18o	AlCl$_2$	SiMe$_3$	Et	I		91
18p	AlCl$_2$	SiMe$_3$	N(SiMe$_3$)$_2$	Cl		105
18q	AlCl$_2$	SiMe$_3$	EtN—N═N—NEt			91
18r	AlCl$_2$	SiMe$_3$	tBuN—N═N—N-tBu			91
18s	AlCl$_2$	SiMe$_3$	N(SiMe$_3$)$_2$	N$_3$		91
18t	AlCl$_2$	SiMe$_3$	Cl	Cl		91
18u	AlBr$_2$	SiMe$_3$	Br	Br		91
18v	AlI$_2$	SiMe$_3$	I	I		91
18w	GaMe$_2$	SiMe$_3$	Ph	Ph		102
18x	InMe$_2$	SiMe$_3$	Ph	Ph		102
18y	GeCl$_2$	tBu	═S	Cl		106
18z	SnMe$_2$	tBu	H	BH$_3$		95
18aa	SnMe$_3$	Me	Me	tBu		107a
18ab	SnCl	SiMe$_3$	N(SiMe$_3$)$_2$	Cl		105
18ac	SnCl$_3$	SiMe$_3$	Me	N(SiMe$_3$)$_2$		104,107b,108
18ad	TiCl$_2$	SiMe$_3$	Me	N(SiMe$_3$)$_2$		104,107b,108
18ae	TiCl$_3$	SiMe$_3$	N(SiMe$_3$)$_2$	Cl	+	105
18af	TiCl$_3$	SiMe$_3$	CCl$_3$	Cl	+	109
18ag	TiCl$_3$(MeCN)	SiMe$_3$	Ph	Ph	+	110a
18ah	TiCl$_2$[NPPh$_2$N(SiMe$_3$)$_2$]	SiMe$_3$	Ph	Ph	+	110a
18ai	[TiCl$_2$(MeCN)	(SiMe$_3$)$_{1/2}$	Ph	Ph]$_2$	+	110a
18aj	Zr(Cp)$_2^+$(MeCN)	SiMe$_3$	H	N(SiMe$_3$)$_2$		110b
18ak	Zr(Cp)$_2$H	SiMe$_3$	H	N(SiMe$_3$)$_2$		110b
18al	Zr(Cp)$_2$Cl	SiMe$_3$	H	N(SiMe$_3$)$_2$		110b
18am	Zr(Cp)$_2$OTf	SiMe$_3$	H	N(SiMe$_3$)$_2$		110b
18an	ZrCl$_3$	SiMe$_3$	Me	N(SiMe$_3$)$_2$		111a
18ao	ZrCl$_3$(Thf)	SiMe$_3$	Me	N(SiMe$_3$)$_2$	+	111a,b
18ap	ZrCl$_3$(OPPh$_3$)	SiMe$_3$	Me	N(SiMe$_3$)$_2$		111a
18aq	ZrCl$_3$(MeCN)	SiMe$_3$	Ph	Ph	+	112
18ar	ZrCl$_4^-$	SiMe$_3$	Ph	Ph	+	113
18as	NbCl$_4$	SiMe$_3$	N(SiMe$_3$)$_2$	Cl		105
18at	Mn(CO)$_3$	SiMe$_3$	N(SiMe$_3$)$_2$	OMe		114
18au	Mn(CO)$_3$	SiMe$_3$	N(SiMe$_3$)$_2$	OPh	+	114,115
18av	Mn(CO)$_3$	SiMe$_3$	N(SiMe$_3$)$_2$	Cl		114
18aw	Mn(CO)$_3$	SiMe$_3$	N(SiMe$_3$)$_2$	Br		114–116
18ax	Mn(CO)$_4$	SiMe$_3$	N(SiMe$_3$)$_2$	Br		114,115
18ay	Re(CO)$_3$	SiMe$_3$	CH$_2$SiMe$_3$	N(SiMe$_3$)$_2$	+	117
18az	Re(CO)$_2$(CN-tBu)$_2$	SiMe$_3$	CH$_2$SiMe$_3$	N(SiMe$_3$)$_2$		117
18ba	Re(CO)$_2$[P(OMe)$_3$]$_2$	SiMe$_3$	CH$_2$SiMe$_3$	N(SiMe$_3$)$_2$		117
18bb	Re(CO)$_4$	SiMe$_3$	N(SiMe$_3$)$_2$	Cl		118
18bc	Re(CO)$_4$	SiMe$_3$	═Mn(CO)$_2$Cp		+	119
18bd	[Re(CO)$_4$	SiMe$_3$	(NSiMe$_3$)$_{1/2}$	(NSiMe$_3$)$_{1/2}$]$_2$	+	118
18be	FeCl$_2$	SiMe$_3$	N(SiMe$_3$)$_2$	Cl		105
18bf	Ni(π-C$_3$H$_5$)	SiMe$_3$	CH$_2$CH═CH$_2$	N(SiMe$_3$)$_2$		120
18bg	Pd(π-C$_3$H$_5$)	SiMe$_3$	CH$_2$CH═CH$_2$	N(SiMe$_3$)$_2$	+	120
18bh	PtCl(π-C$_2$H$_4$)	Me	Me	Me		121
18bi	ZnPh	SiMe$_3$	Ph	N(SiMe$_3$)$_2$	+	101,122,123
18bj	ZnPh(Py)	SiMe$_3$	Ph	N(SiMe$_3$)$_2$		101,122
18bk	ZnPh(OPPh$_3$)	SiMe$_3$	Ph	N(SiMe$_3$)$_2$		101,122
18bl	Ce(Cot)	SiMe$_3$	Ph	Ph		124
18bm	Pr(Cot)	SiMe$_3$	Ph	Ph		124
18bn	Nd(Cot)	SiMe$_3$	Ph	Ph		124
18bo	Sm(Cot)	SiMe$_3$	Ph	Ph		124

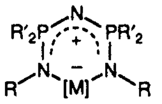
Table 14. Bis($1,3,2\lambda^5,4$-diazaphospha)metallaspiro[3.3]-bicycloheptanes



19

no.	[M]	R	R′	R″	X-ray	ref(s)
19a	(Na	$SiMe_3$	Ph	$Ph)_2^-$	+	97
19b	$SnCl_2$	Me	Me	Me		125
19c	Zn	$SiMe_3$	Ph	$N(SiMe_3)_2$		101,122
19d	PrCl	$SiMe_3$	Ph	$N(SiMe_3)_2$		126
19e	NdCl	$SiMe_3$	Ph	Ph		126
19f	SmI_2^-	$SiMe_3$	Ph	Ph	+	96
19g	$Yb(Thf)_2$	$SiMe_3$	Ph	Ph		96
19h	$ThCl_2$	$SiMe_3$	Ph	Ph		126
19i	UCl_2	$SiMe_3$	tBu	tBu		126
19j	UCl_2	$SiMe_3$	Ph	Ph		126
19k	UO_2	$SiMe_3$	Ph	Ph		126

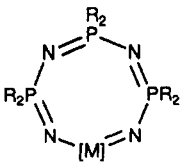
Table 15. Zwitterionic Chelates with a Cationic N_3P_2 Backbone



28

no.	[M]	R	R′	X-ray	ref
28a	$AlMe_2$	$SiMe_3$	Ph	+	133
28b	$AlMe_2$	$SiMe_3$	NMe_2		133
28c	$GaMe_2$	$SiMe_3$	Ph		133
28d	$GaMe_2$	$SiMe_3$	NMe_2		133
28e	$InMe_2$	$SiMe_3$	Ph	+	133
28f	$InMe_2$	$SiMe_3$	NMe_2		133
28g	$SbCl_4$	H	Ph		134a
28h	$Sb(O_2CMe)_2$	$SiMe_3$	NMe_2		134b
28i	ZnMe	$SiMe_3$	Ph		135
28j	ZnEt	$SiMe_3$	Ph		135
28k	$Zn[N(SiMe_3)_2]$	$SiMe_3$	Ph	+	135

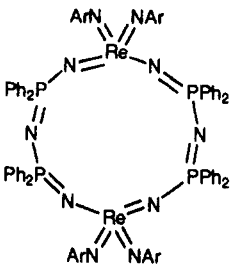
Only one authentic example of a $1,3,5,7,2\lambda^5,4\lambda^5,6\lambda^5,8$-tetraazatriphosphametallocine **36a** has been isolated thus far. Its structure has been derived from mass and multinuclear magnetic resonance spectroscopy.[164] The other, **36b**, has been detected in the mass spectrum of a linear ionic precursor.[168] Similar behavior has been found with intermediates in the formation of several compounds **34**.[165a]



36a: [M] = VCl_2, R = CF_3
b: [M] = WCl_3, R = Ph

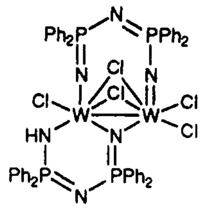
Eight-membered cyclophosphazenes containing two metal atoms **37** are listed in Table 20.

A twelve-membered heterocycle **38** has been found as a byproduct in the synthesis of **35** and was characterized by X-ray analysis. Its genesis can be understood as a topological dimerization of **35**, which represents a new reaction type in phosphazene chemistry.[166]



38: Ar = 2,6-$iPr_2C_6H_3$

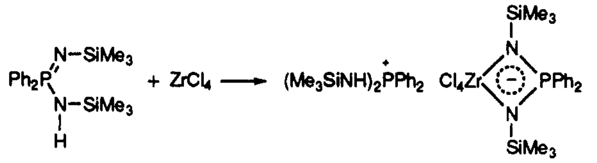
The only example of a metallacyclophosphazene, where the metal is not in its formally highest oxidation state, is bimetallic **39** with W^{6+} and W^{5+}, respectively. The X-ray structure shows one N and two Cl bridges and a W–W bonding interaction.[173]



39

C. Synthetic, Theoretical, and Structural Aspects

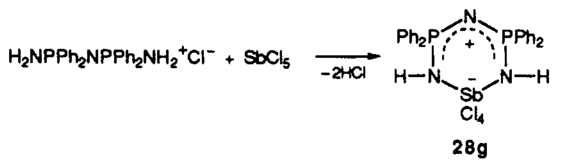
Three major types of reactions have found application in the syntheses of diazadiphosphametallidines **17–19** (i) the abstraction of alkali or trimethylsilyl halides from metal halides and the corresponding aminoiminophosphorus precursors, (ii) elimination of a stable hydrocarbon from alkyl- or aryl-substituted metals, and (iii) oxidation of stable or intermediate P^{III} heterocycles, in the latter case with migration of metal or nitrogen bound groups. The attempt of hydrogen chloride elimination led in one case to the formation of a salt with the hitherto unknown bis[(trimethylsilyl)amino]-diphenylphosphonium cation.[113]



18ar (6)

The transition metals forming four-membered N_2-PM rings have been found limited thus far to group 4 metals and Nb in their highest oxidation states, group 7 metals in the oxidation state +1, and groups 8–12, lanthanoid, and actinoid elements in their most stable oxidation states.

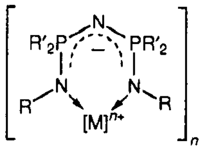
Precursors with a N_3P_2 backbone and metals unlikely to form multiple bonds yield zwitterionic six-membered heterocycles, e.g.[134] **28g**.



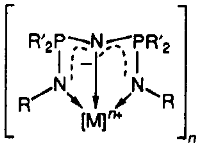
28g (7)

while the lower homologues phosphorus,[174] arsenic[175]

Table 16. Zwitterionic Chelates with an Anionic N_3P_2 Backbone



29A



29B

no.	[M]	type[a]	n	R	R′	X-ray	ref(s)
29a	$\mathrm{Li^+}$		1	$\mathrm{SiMe_3}$	Ph		133,136
29b	$\mathrm{Li^+}$		1	$\mathrm{SiMe_3}$	$\mathrm{NMe_2}$		136
29c	$\mathrm{Na^+}$			$\mathrm{SiMe_3}$	Ph		133
29d	$\mathrm{(Na^+}$	B	1	$\mathrm{SiMe_3}$	$\mathrm{NMe_2)_2}$	+	136,137
29e	$\mathrm{K^+}$		1	$\mathrm{SiMe_3}$	Ph		133
29f	$\mathrm{(K^+}$	B	1	$\mathrm{SiMe_3}$	$\mathrm{NMe_2)_\infty}$	+	136,137
29g	$\mathrm{(Rb^+}$	(B)	1	$\mathrm{SiMe_3}$	$\mathrm{NMe_2)_\infty}$		136
29h	$\mathrm{(Cs^+}$	(B)	1	$\mathrm{SiMe_3}$	$\mathrm{NMe_2)_\infty}$		136
29i	$\mathrm{Ca^{2+}}$	B	2	$\mathrm{SiMe_3}$	$\mathrm{NMe_2}$	+	137
29j	$\mathrm{Ba^{2+}}$	B	2	$\mathrm{SiMe_3}$	$\mathrm{NMe_2}$	+	138
29k	$\mathrm{Cu^{2+}}$	(A)	2	H	Ph		139,140
29l	$\mathrm{(Li^+}$	A	1	$\mathrm{SiMe_3}$, H	$\mathrm{Ph)_2}$	+	136

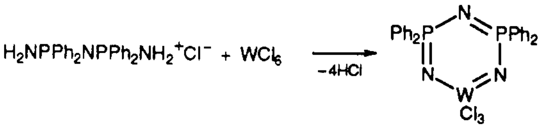
[a] The type of complex A or B has been assigned, those in parentheses are tentatively according to electronic properties of the metal atoms.

Table 17. η^n-N-Coordinated Cyclophosphazene Complexes

$$[\mathrm{M}]\cdot\eta^n(\mathrm{NPR_2})_x$$

no.	[M]	η^n	x	R	X-ray	ref(s)
32a	$\mathrm{Cr(CO)_3}$	η^3-1,3,5	3	Cl		141
32b	$\mathrm{Mo(CO)_4}$	η^3-1,3	4	Me		143
32c	$\mathrm{Mo(CO)_3}$	η^3-1,3,5	4	Me	+	144,145a
32d	$\mathrm{W(CO)_3}$	η^3-1,3,5	4	Me		145a
32e	$\mathrm{NiCl_2}$	η^2-1,5	4	NHMe		145b
32f	$\mathrm{PtCl_2}$	η^2-1,5	4	Me	+	146,147
32g	$\mathrm{PtCl_2}$	η^2-1,5	4	NHMe	+	148
32h	$\mathrm{Mo(CO)_3}$	η^3-1,3,5	5	Me		145a
32i	$\mathrm{W(CO)_3}$	η^3-1,3,5	5	Me		145a
32j	$\mathrm{MnCl^+}$	η^4-1,3,7,9	6	$\mathrm{NMe_2}$		142
32k	$\mathrm{Mn(\eta^2\text{-}NO_3)^+}$	η^4-1,3,7,9	6	$\mathrm{NMe_2}$		142
32l	$\mathrm{FeCl^+}$	η^4-1,3,7,9	6	$\mathrm{NMe_2}$		142
32m	$\mathrm{CoCl^+}$	η^4-1,3,7,9	6	$\mathrm{NMe_2}$	+	142,149,150
32n	$\mathrm{Co(\eta^2\text{-}NO_3)^+}$	η^4-1,3,7,9	6	$\mathrm{NMe_2}$		142
32o	$\mathrm{NiCl^+}$	η^4-1,3,7,9	6	$\mathrm{NMe_2}$		142
32p	$\mathrm{NiBr^+}$	η^4-1,3,7,9	6	$\mathrm{NMe_2}$		142
32q	$\mathrm{Ni(\eta^2\text{-}NO_3)^+}$	η^4-1,3,7,9	6	$\mathrm{NMe_2}$		151
32r	$\mathrm{PdCl_2}$	η^2-1,5	6	Me	+	151
32s	$\mathrm{PtCl_2}$	η^2-1,5	6	Me		151
32t	$\mathrm{CuCl^+}$	η^4-1,3,7,9	6	$\mathrm{NMe_2}$	+	152,153
32u	$\mathrm{Cu(\eta^2\text{-}NO_3)^+}$	η^4-1,3,7,9	6	$\mathrm{NMe_2}$		142
32v	$\mathrm{ZnCl^+}$	η^4-1,3,7,9	6	$\mathrm{NMe_2}$		142
32w	$\mathrm{Zn(\eta^2\text{-}NO_3)^+}$	η^4-1,3,7,9	6	$\mathrm{NMe_2}$		142
32x	$\mathrm{Co(\eta^2\text{-}NO_3)^+}$	η^4-1,3,7,9	8	Me	+	154

and group 5–7 metals form conjugated systems via several acyclic and cyclic intermediates, e.g.[4]

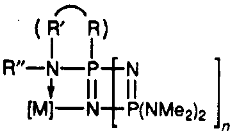


$\mathrm{H_2NPPh_2NPPh_2NH_2{}^+Cl^-} + \mathrm{WCl_6} \xrightarrow[-4\mathrm{HCl}]{}$ (8)

34r

Instead of the above phosphazenium salt[176,177] silylated $\mathrm{(Me_3Si)_2N{-}PPh_2{=}N{-}PPh_2{=}NSiMe_3}$[132] or alkali salts **29a,c,e**[133,136] can be employed as precursors for ring formation.

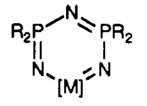
Table 18. Complexes of Aminocyclophosphazenes with η^2-Exo/Endo Bonding



33

no.	[M]	n	R	R′	R″	X-ray	ref(s)
33a	$\mathrm{Mo(CO)_4}$	2	$\mathrm{-NH(CH_2)_2-}$		H		81a
33b	$\mathrm{W(CO)_4}$	2	$\mathrm{-NH(CH_2)_3-}$		H		81a
33c	$\mathrm{Mo(CO)_4}$	3	$\mathrm{NMe_2}$	Me	Me		145a
33d	$\mathrm{W(CO)_4}$	2	$\mathrm{-NH(CH_2)_2-}$		H		81a
33e	$\mathrm{W(CO)_4}$	2	$\mathrm{-NH(CH_2)_3-}$		H		81a
33f	$\mathrm{W(CO)_4}$	3	$\mathrm{NMe_2}$	Me	Me	+	145a,155,156
33g	$\mathrm{PdCl_2}$	2	$\mathrm{-NH(CH_2)_3-}$		H		81a

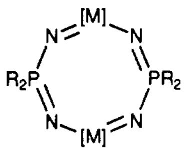
Table 19. 1,3,5,2λ^5,4λ^5,6λ^n-Triazadiphosphametallines



34

no.	[M]	R	X-ray	ref(s)
34a	$\mathrm{Se^\bullet}$	Ph		158
34b	SeCl	Ph	+	136,158,159
34c	$\mathrm{VCl_2}$	Me		160
34d	$\mathrm{VCl_2}$	$\mathrm{CF_3}$	+	161,162
34e	$\mathrm{VCl_2}$	Ph	+	163,164
34f	$\mathrm{VCl_2}$	$\mathrm{N(C_2H_4)_2O}$		165a
34g	$\mathrm{VBr_2}$	Ph		165b
34h	$\mathrm{NbCl_2}$	Ph		167
34i	$\mathrm{MoCl_3(MeCN)}$	Ph	+	167
34j	$\mathrm{MoCl_3}$	$\mathrm{4\text{-}ClC_6H_4}$		160
34k	$\mathrm{MoCl_2(N_3)}$	Ph		165c
34l	$\mathrm{MoCl_2(NMe_2)}$	Ph		165c
34n	$\mathrm{MoCl_2(NEt_2)}$	Ph		165c
34o	$\mathrm{MoCl_3}$	$\mathrm{N(C_2H_4)_2O}$		165a
34p	$\mathrm{WF_3}$	Ph		163
34q	$\mathrm{WCl_3}$	Me		160
34r	$\mathrm{WCl_3(MeCN)}$	Ph	+	4,167
34s	$\mathrm{WCl_3}$	$\mathrm{NMe_2}$		165a
34t	$\mathrm{WCl_3}$	$\mathrm{N(C_2H_4)_2O}$		165a
34u	$\mathrm{WBr_3}$	Ph		163
34v	$\mathrm{ReO_2}$	Ph		166
34w	$\mathrm{ReCl_4}$	Ph		163
34x	$\mathrm{ReCl_4}$	$\mathrm{4\text{-}ClC_6H_4}$		160

Table 20. 1,3,5,7,2λ^5,6λ^5,4,8-Tetraazadiphosphadimetallocines

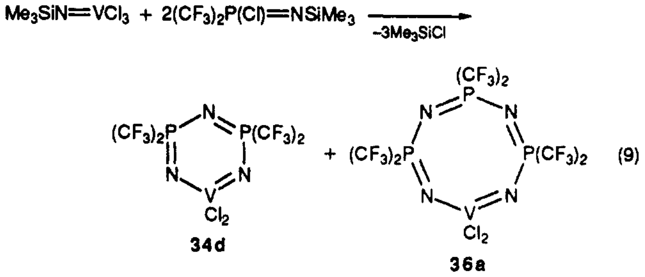


37

no.	[Me]	R	X-ray	ref(s)
37a	SeMe	Ph	+	169
37b	SeEt	Ph		169
37c	SePh	Ph		169,170
37d	[Se(Se-bridge)	$\mathrm{Ph]_2}$		169
37e	$\mathrm{VCl_2}$	$\mathrm{C_2F_5}$	+	164
37f	$\mathrm{VCl_2}$	Ph		112
37g	$\mathrm{VCl(OSiMe_3)}$	Ph	+	171
37h	$\mathrm{WCl_3(Thf)}$	Ph	+	172

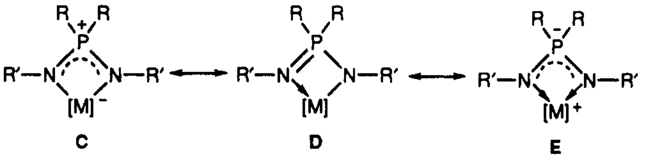
In the case of hydrogen chloride labile amino substituents on phosphorus, metal nitride precursors have been employed in the synthesis of **34f,o,s,t** with elimination of $\mathrm{NH_4Cl}$.[11,165a]

Different reactivity has been found with iminochlorophosphoranes and $Cl_3V{=}X$ compounds: While, with R = C_2F_5 or Ph, X = $NSiMe_3$, tetraazadiphosphadimetallocines **37e,f** are formed via [2 + 2 + 2 + 2] cycloaddition,[112,164] only one metal is incorporated in the heterocycles **34d**[161] and **36a**,[164] with R = CF_3, X = $NSiMe_3$, and **34e**, with R = Ph, X = O, respectively.[164] The solid perfluoroalkyl compounds **34d**, **36a**, and **37e** are the first examples of volatile metallacyclophosphazenes; all others are solids with high melting points.



Ring formation without changes in the environment at phosphorus is paralleled with a low-field shift in the ^{31}P NMR spectra as compared to the hypothetical starting materials for most of the compounds. Only with heavier group 1 and 2 metals and in the case of unsaturated compounds **34b**[136,158] and eight-membered divanadium compounds **37e–g**[112,164,171] high-field shifts have been observed, while ditungsten compound **37a**[172] shows normal behavior. Higher electronegativity of the substituents at the metals and increasing atomic number in one group causes a high-field shift in the unsaturated heterocycles **34** and main group compounds. As expected, the lanthanoid and actinoid atoms in **19d–j** exert a strong paramagnetic influence on the ^{31}P nucleus (Table 21).

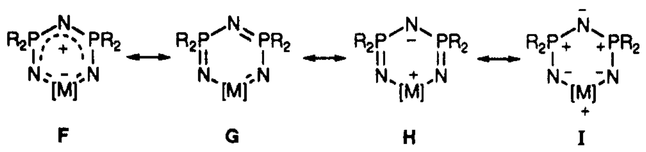
This difference in behavior can be rationalized by an inversion of polarization as seen in the following canonical formulas **C–E** for the four-membered rings of **18** (only one of two resonance forms of **D** is shown).



While rings with transition and group 13–16 metals in high oxidation states are best represented by resonance structure **C**, **E** is the most likely form for group 1 and 2 metals. This is also valid for six-membered chelates **28** and **29**. No assignment can be made for manganese and rhenium carbonyls **18at–bd**, and group 10 complexes **18bf–bh** might be represented best by resonance structure **D**, as well as lanthanoid and actinoid chelates **19d–k**. X-ray structure determinations have been carried out for several complexes **17–19**. No significant trend can be seen in the P–N and M–N bond distances. The P–N distances have been found pairwise almost equal between 158–162 pm in the range of P–N bonds in cyclic phosphazenes.[179] The M–N distances are also pairwise equal, lying in between single and coordinative bonds. One exception has been found in Sm spirocycle **19f**, where each ring contains one short (ca. 239 pm) and one long bond (ca. 250 pm), which are representative of Sm–N single and coordinative bonds.[96]

The P–N bonds in P_2N_3 chelates **28** and **29** have been found in the same range of ca. 160 pm, in contrast to $H_2NPPh_2NPPh_2NH_2^+Cl^-$, where the terminal bonds are longer (ca. 164 pm) and the central bonds are shorter,[180a] and to $Me_3SiN{=}PPh_2{-}N{=}PPh_2{-}N(SiMe_3)_2$, with alternating short and long bonds.[132]

Several resonance structures can be formulated for the unsaturated heterocycles **34–38** exemplarily shown for six-membered rings (one possible resonance form **G′** is omitted).



The P–N bonds adjacent to the metal center in the structurally characterized compounds **34d,e,i,r** have been found to be longer than those in opposition and the M–N bonds are shorter than calculated M–N double bonds, thus favoring the canonical structure **F**. Ab initio SCF calculations performed on **34d** (R = CF_3, [M] = VCl_2) by M. Ehrig and R. Ahlrichs[162] show the electronic structure of **34d** to harmonize best with canonical form **I** with tetravalent P^+ and divalent N^- atomic states. The nitrogen lone pairs are partially delocalized into low-lying orbitals of neighboring atoms, additional stabilization is effected by strong Coulomb interactions. As in the case of phosphazenes, no aromaticity can be attributed to these heterocycles.

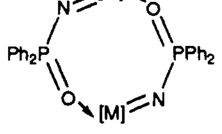
Eight-membered dimetallacyclotetraphosphazene **37g** represents one of the rare examples of a planar eight-membered ring whose structure has been determined.[171]

V. Heteroelements Other than Metals in the Ring Skeleton

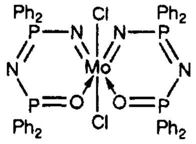
This chapter can be subdivided into two parts, the heteroelement replacing nitrogen adjacent to the metal in phosphazene units and the heteroatomic group being away from the metal. Only compounds where an unsaturated system remains intact have been included.

A. Metal Bound to One Element Other than Nitrogen

Only two types of oxygen-containing metallaheterocycles have been synthesized so far (**40** and **41**). The X-ray analyses of both suggest that the oxygen atom acts as a donor, thus leading to species with metal–nitrogen double bonds.



40a: [M] = $TiCl_2$
b: [M] = CpTiCl
c: [M] = $NbCl_3$



41

The eight-membered system **40a** is isoelectronic with the vanadium compound **37f**, the Ti=N bonds of

Table 21. Selected ^{31}P NMR Shifts

no.	compound	δ (ppm)	Δδ (ppm)	ref(s)
	$Me_3SiN{=}P{-}N(SiMe_3)_2 \triangleq L^1SiMe_3$	325.5		91
17c	$AlCl_2L^1$	279.3	+53.8	91,93
	$Me_3SiN{=}PPh_2N(SiMe_3)_2 \triangleq L^2$	7.6		68
18a	$LiL^2(Thf)_2$	9.4	+1.8	96
19a	$[Na(L^2)_2]^-$	8.6	+1.0	97
18b	$KL^2(Thf)_4$	4.1	−3.5	97
18d	$(CsL^2)_\infty$	1.0	−6.6	97
18ag	$TiCl_3L^2(MeCN)$	25.0	+18.4	110a
18aq	$ZrCl_3L^2(MeCN)$	38.8	+31.2	112
19e	$NdCl(L)_2^2$	−163.9	−171.5	126
19f	$[SmI_2(L^2)_2]^-$	70.6	+63.0	96
19h	$ThCl_2(L^2)_2$	17.4	+9.8	126
19j	$UCl_2(L^2)_2$	−230.4	−238.0	126
19k	$UO_2(L^2)_2$	42.9	+35.3	126
	$Me_3SiN{=}P(Me)N(SiMe_3)_2NHSiMe_3 \triangleq L^3H$	6.3		104
18g	$AlMe_2L^3$	32.9	+26.6	98
18n	$AlCl_2L^3$	34.4	+28.1	98
18ac	$SnCl_3L^3$	39.6	+33.3	104
18ad	$TiCl_3L^3$	24.4	+18.1	104
18an	$ZrCl_3L^3$	25.6	+19.3	111a
	$Me_3SiN{=}P(Ph)N(SiMe_3)_2NHSiMe_3 \triangleq L^4H$	2.2		104
18m	$AlPh_2L^4$	27.9	+25.7	98
18bi	$ZnPhL^4$	26.7	+24.5	101,122
19c	$Zn(L^4)_2$	24.7	+22.5	122
	$(Me_3SiNPPh_2)_2NH \triangleq L^5H$	11.1		132
29a	LiL^5	11.3	+0.2	136
29c	NaL^5	5.9	−5.4	136
29e	KL^5	0.7	−10.6	136
28a	$AlMe_2L^5$	23.4	+12.3	133
28c	$GaMe_2L^5$	22.0	+10.7	133
28d	$InMe_2L^5$	17.6	+6.3	133
28i	$ZnMeL^5$	17.6	+6.3	135
28k	$ZnN(SiMe_3)_2L^5$	20.8	+9.5	135
	$[Me_3SiNP(NMe_2)_2]_2NH \triangleq L^6H$	17.4		136
29b	LiL^6	17.2	−0.2	136
29d	$(NaL^6)_2$	9.8	−7.6	136,137
29f	$(K\,L^6)_\infty$	6.4	−11.0	136,137
29h	$(CsL^6)_\infty$	3.3	−14.1	136
29i	$Ca(L^6)_2$	18.7	+1.3	137
29j	$Ba(L^6)_2$	5.2	−12.2	138
28b	$AlMe_2L^6$	23.1	+5.7	133
28f	$InMe_2L^6$	20.3	+2.9	133
28h	$Sb(OAc)_2L^6$	25.6	+8.2	134b
	$(HNPPh_2)_2NH \triangleq L^7H_3$	17.7		178
34b	$SeClL^7$	12.5	−5.2	136,158
34e	VCl_2L^7	43.7	+26.0	163,164
34i	$MoCl_3L^7$	44.6	+26.9	167
34k	$MoCl_2(N_3)L^7$	30.0	+12.3	165c
34n	$MoCl_2(NEt_2)L^7$	24.7	+7.0	165c
34p	WF_3L^7	22.5	+4.8	163
34r	WCl_3L^7	39.2	+21.5	4
34u	WBr_3L^7	43.8	+26.1	163
34w	$ReCl_4L^7$	46.2	+28.5	163
	$Me_3SiN{=}PPh_2N(SiMe_3)_2 \triangleq L^8(SiMe_3)_3$	7.6		168
37a	$(SeMeL^8)_2$	33.6	+26.0	169
37c	$(SePhL^8)_2$	21.7	+14.1	169
37f	$(VCl_2L^8)_2$	−10.2	−17.8	112
37g	$[VCl(OSiMe_3)L^8]_2$	−12.6	−20.2	171
37h	$(WCl_3L^8)_2$	36.7	+29.1	172

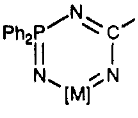
40a·4MeCN are among the shortest known so far.[112] While the synthesis of **40a–c** proceeds straightforward from the appropriate metal halide and a silylated phosphinic acid imine,[112,180b] the synthesis of **41** proceeds in low yields from molybdenum oxide halides and a N_3P_2 acyclic precursor via formal loss of NH_4Cl. Surprisingly, the ^{31}P NMR spectrum shows only one signal for the two sets of inequivalent phosphorus atoms.[181]

Several chromium tetracarbonyl complexes with CPNP ligands have been synthesized giving five-membered C,P-chelates.[24]

B. Heteroelements Nonadjacent to the Metal

A subdivision can be made between heteroatoms replacing phosphorus and (a group of) heteroatoms replacing nitrogen opposite to the metal in the six-

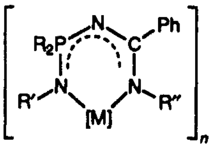
Table 22. Conjugated 1,3,5,2λ^5,4λ^n-Triazaphosphametallines



42

no.	[M]	R	X-ray	ref(s)
42a	Se$^\bullet$	Ph		158
42b	SeCl	Ph	+	136,158,182
42c	SeCl	C_6H_4-pCF$_3$	+	160
42d	SeCl	C_6H_4-mCF$_3$		160
42e	TeCl(Py)	C_6H_4-pCF$_3$	+	113
42f	[Mo(O)Cl	Ph]$_2$		183
42g	MoCl$_2$O-tBu	Ph		160
42h	ReO$_2$	Ph		166
42i	ReO$_2$	C_6H_4-pCF$_3$	+	166

Table 23. Non Conjugated 1,3,5,2λ^5,4λ^n-Triazaphosphametallines



43

no.	[M]	R	R′	R″	n	X-ray	ref
43a	Se	Ph	**42a**		1	+	158
43b	TiCl$_2$	Ph		tBu	1		183
43c	Pt(PPh$_3$)$_2$	Ph		SiMe$_3$	1		182
43d	Pt(PPh$_3$)$_2^+$	Ph	H	H	1	+	182
43e	Pt	Me	Me	Me	2		184

membered rings, **34**. The first group consists of conjugated, **42**, and nonconjugated triazaphosphametallines, **43**, which are listed in Tables 22 and 23.

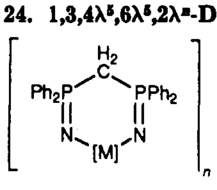
The X-ray structure determinations of **42b,c,e,i** show the rings being essentially planar. Compound **42e** contains one of the rare examples of a Te=N double bond.[113] The ^{31}P NMR spectra of **42b–h** show significant low-field shifts compared to the starting materials. Reduction of **42b** with SbPh$_3$ in CH$_2$Cl$_2$ affords a species giving a persistent ESR signal, **42a**. Its electronic structure is best described with a positive charge on phosphorus and the negative charge and the unpaired electron delocalized over the rest of the ring.[158]

Unlike its sulfur congener, radical **42a** dimerizes in hot MeCN not by forming a Se–Se bond, instead a Se–N bond is obtained leaving **43a**, whose X-ray structure shows both rings nonplanar.[158] Due to mechanistic reasons, structure **43b** is favored over isomers with the tBu group at one of the other nitrogen atoms,[183] as it is seen in **43c**, which can be cautiously hydrolized to yield cationic **43d**, whose X-ray structure has been determined with Cl$^-$ as an anion. The ring adopts a half-boat conformation with Pt being distorted square planar.[182]

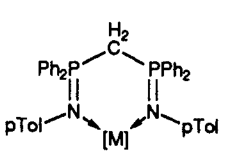
A somewhat greater variety of heteroatoms has been found able to replace the nitrogen opposite to metal. Starting from a bis(iminophosphoranyl)methane a series of nonconjugated diazadiphosphametallines **44** and **45** has been synthesized (Table 24).

The ring closure causes a downfield shift of the ^{31}P NMR signals in **44** compared to the starting material, the effect is stronger in the transition metal compounds **44f–i**. The X-ray structure of **44f**·Cl$^-$ shows the ring being nonplanar.[113]

Table 24. 1,3,4λ^5,6λ^5,2λ^n-Diazadiphosphametallines



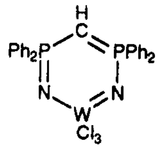
44



45

no.	[M]	n	X-ray	ref(s)
44a	Ge(N$_3$)$_2$	1		185
44b	GeCl$_2$	1		185
44c	Ge	2		185
44d	SeCl$_2$	1		186
44e	TeCl$_2$	1		186
44f	VCl$_2$(Py)$_2^+$	1	+	113
44g	WF$_4$	1		186
44h	WCl$_4$	1		186
44i	OsO$_2$(OSiMe$_3$)$_2$	1		187
45a	Rh(CO)$_2^+$			188a,b
45b	RhCod$^+$			188a,b

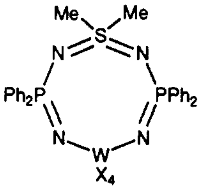
Compound **44h** can be dehydrohalogenated with Dbu to yield the conjugated heterocycle **46**.



46

The delocalization causes a further downfield shift in the ^{31}P NMR spectrum of **46** compared to that of **44h**.[186]

Formal replacement of nitrogen by a sulfodiimide unit leads to eight-membered heterocycles **47**.

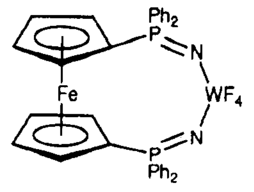


47a: X = F
b: X = Cl

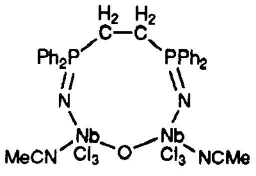
The X-ray structure of **47a** shows a distorted eight-membered ring with considerable multiple-bond participation in the W–N bonds.[189]

Compound **48a** can be considered as an "inverse cryptand" with one metal in a high oxidation state and one in a medium oxidation state. The structure has been confirmed by mass and ^{19}F and ^{31}P NMR spectroscopy.[190]

A nine-membered ring **48b** with a distorted ring geometry is available from a bissilylated bis(iminophosphoranyl)ethane and NbCl$_5$ in Thf. The oxygen probably arose from solvent cleavage. The Nb–N bonds show partial multiple bonding.[191a]

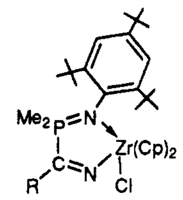


48a



48b

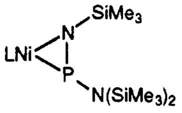
Five-membered heterocycles containing carbon, **49a–c**, have been generated by trapping the intermediate of the reaction of dimethylzirconocene with a *P*-chloroiminophosphane with nitriles.[191b] The cyclic structure is consistent with NMR spectra.



49a: R = Me
b: R = iPr
c: R = Ph

VI. Metal Bound to Phosphorus and Nitrogen

Only a few cycles known so far have metal fragments neighboring phosphorus and nitrogen atoms. Two Ni^0 complexes **50a,b** have been reported where the ligand $Me_3SiN{=}PN(SiMe_3)_2$ has been formulated as π-bonded.[16,17] In analogy to other ligands with heteropolar double bonds, e.g. hexafluoroacetone[192] and from the X-ray structure data of **50a** (Ni–P ≈ 223 pm, Ni–N ≈ 191 pm, and P–N ≈ 165 pm),[16] a three-membered ring as depicted with Ni^{2+} seems to be more likely.



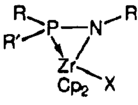
50a: L = Dppe
b: L = Cod

J.-P. Majoral and co-workers have investigated reactions of zirconocene compounds with iminophosphanes[110b,193,194] resulting, via hydride or methanide migration from Zr to P, in azaphosphazirconiridines **51** listed in Table 25.

The X-ray structure of **51b**[194] and the P–H coupling constants of **51b–g** are consistent with three-membered rings instead of open-chain compounds.[110b,194] Compounds **51e–g** have been generated by chlorine exchange in **51b**.[110b,194]

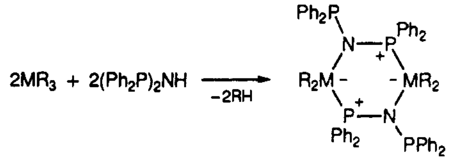
While tetraphenyldiphosphazane reacts with gallium trialkyls to form symmetric eight-membered heterocycles **6a,b**, a different behavior has been found with aluminum trialkyls and gallium trimethyl, the latter forming both isomers. Zwitterionic 1,4,2,5,3,6-diazadiphosphadimetallines **52a–c** are formed; the structure has been proven by ^1H and ^{31}P NMR spectroscopy and an X-ray analysis for **52a**, which, from bond lengths, favors the depicted charge separation over coordinative bonds and a P=N double bond.[63,195]

Table 25. Three-Membered P-N-Zr Heterocycles



51

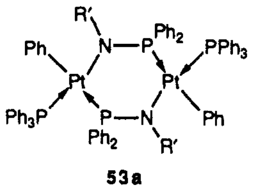
no.	X	R	R′	R″	X-ray	ref(s)
51a	Me	$(Me_3Si)_2N$	Me	$SiMe_3$		110b
51b	Cl	$(Me_3Si)_2N$	H	$SiMe_3$	+	110b,193,194
51c	Cl	$(Me_3Si)tBuN$	H	tBu		110b
51d	Cl	Tmpip	H	$SiMe_3$		110b
51e	$(NCMe)^+$	$(Me_3Si)_2N$	H	$SiMe_3$		110b,194
51f	OTf	$(Me_3Si)_2N$	H	$SiMe_3$		110b,194
51g	N_3	$(Me_3Si)_2N$	H	$SiMe_3$		110b



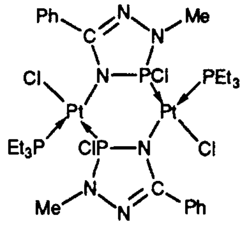
(10)

52a: M = Al, R = Me
b: M = Al, R = Et
c: M = Ga, R = Me

Similar six-membered rings **53a,b** are available by insertion of nitrenes into the Pt–P bond of $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ with migration of a phenyl group[196] and by insertion of a 1*H*-1,2,4,5-triazaphosphole into a Pt–Cl bond of $(Et_3P)_2PtCl_2$.[197]

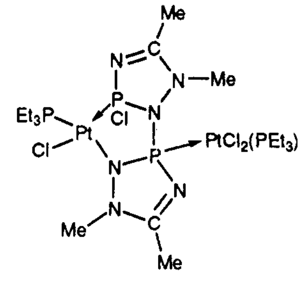


53a



53b

A five-membered heterocycle **54** is formed when a 2*H*-1,2,4,5-triazaphosphole is employed.



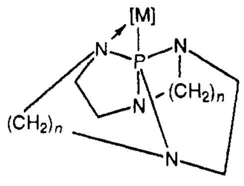
54

The structures of these platinum heterocycles have been assigned unambigously by multinuclear NMR spectroscopy.[197]

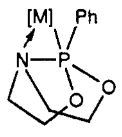
Three-membered MNP chelates **55** and **56** as part of a polycyclic system are available from tetracyclic tetraazaphosphoranes and bicyclic dioxaazaphosphoranes (Table 26).

The X-ray analyses of **55a–c** show the complexed P–N bond to be significantly longer than the other three; in the ^{31}P NMR spectra a downfield shift of ca. 10 ppm is observed compared to the starting materials indicating pentacoordinated phosphorus.[198a] Long P–N bonds

Table 26. Three-Membered P–N Chelates



55

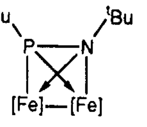


56

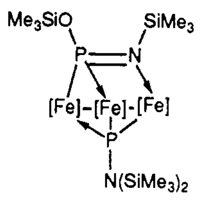
no.	[M]	n	X-ray	ref(s)
55a	$Mo(CO)_2Cp$	2	+	198a
55b	$Co(CO)_3$	2	+	198a,b
55c	$Mo(CO)_2Cp$	3	+	198a,199a
55d	$W(CO)_2Cp$	3		199a
55e	$Pt(PPh_3)Cl$	2	+	199b
55f	$Pt(PR_3)X$	2		199c
56a	$Mo(CO)_2Cp$		+	199d
56b	$W(CO)_2Cp$			199d

and short M–P bonds have also been found in the complexes **56a,b**.[199d]

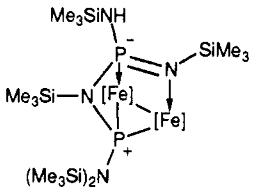
Some compounds containing Fe–Fe bonds **57–60**, where P–N units act as bidentate ligands with partial covalent bonds to the metal atoms ([Fe] = $Fe(CO)_3$), have been synthesized.



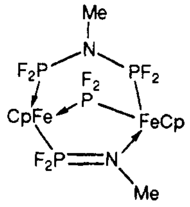
57[200]



58[201]



59[201]



60[62,202]

All compounds have been characterized by X-ray analysis; **58** and **59** have also been characterized by ^1H and ^{31}P NMR spectroscopy. The long P–N bond in **57**[200] and the short P=N bonds in **58**, **59**,[201] and **60**[202] (<160 pm) make the bond orders likely as depicted.

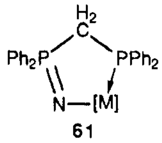
K. V. Katti and R. G. Cavell have described five-membered phosphanomethylene complexes of types **61** and **62**. They are listed in Table 27.

All compounds have been characterized by elemental analyses and multinuclear magnetic resonance spectroscopy; additionally compound **62f** has been investigated by X-ray diffraction.[206]

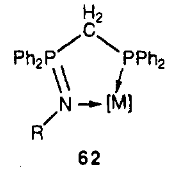
Complexes **61** contain no group R attached to nitrogen and a covalent M–N bond. The M–N bonds in **62** have to be formulated as coordinative bonds.

A distorted tricyclic structure has been found in the lithiation reaction of (phenylamino)diphenylphosphane with nBuLi in Et_2O. The P–N bond distances of **63** lie between single- and double-bond lengths, and the Li–N and Li–P separations are in a range found with similar compounds.[208]

Table 27. Five-Membered Chelates with P and N Atoms Bonded to the Metal

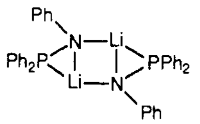


61



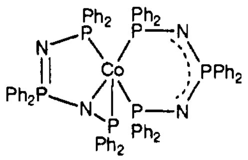
62

no.	[M]	R	X-ray	ref(s)
61a	$ReO_2(OSiMe_3)_2$			185,203
61b	$\{\mu\text{-}O[ReO_2OSiMe_3]_2\}_{1/2}$			185
61c	Rh(Cod)			185,204,205,207
61d	Ir(Cod)			185,204,207
62a	$Mo(CO)_4$	$SiMe_3$		185,204,206,207
62b	$W(CO)_4$	$SiMe_3$		185,204,206,207
62c	Rh(CO)Cl	$SiMe_3$		185,204–206,207
62d	Rh(CO)Cl	C_5F_4N		206,207
62e	Rh(CO)Cl	C_6F_4-pCN		206,207
62f	$PdCl_2$	H	+	206
62g	$PdCl_2$	$SiMe_3$		206
62h	$PdCl_2$	$GeMe_3$		206



63

An interesting tricyclic system **64** has been synthesized from $CoCl_2$ and $LiN(PPh_2)_2$ in an unexpected oxidative scrambling of the P_2N chain.



64

In contrast to the metallacyclophosphazenes **34** with a MN_3P_2 backbone, the X-ray structure of **64** shows the six-membered CoP_3N_2 ring being nonplanar.[209]

VII. Applications and Outlook

This article covers the development of cyclic main group and transition metal containing phosphazanes and phosphazenes. Main emphasis has been put upon synthetic, structural, and NMR spectroscopical aspects. As pointed out in the introduction, the variety of compounds might imply some technical use.

An in situ mixture of the starting materials of complex **18bf**, $Ni(\pi\text{-}C_3H_5)_2$, and $(Me_3SiN{=})_2PN(SiMe_3)_2$ catalyses polymerization of ethene with activities of ca. 1000 mol of ethene per mole of catalyst.[120] Similarly, mixtures of the diiminoaminophosphorane and Ni^0 complexes with cyclic polyene ligands catalyze polymerization of α-olefins to yield 2,ω-polymers.[210]

Rh complex **3af** has been found active in the catalysis of hydrogenation and hydroformylation reactions.[26]

Several complexes **3h,k,l,s,t,u,w,af,ao,aq** and **4g** built up from a $[M]P_2$ moiety serving as a protecting group for asymmetric amino acids have been used in asymmetric syntheses of optically active natural substances, e.g. annelation of amino acids.[26,27,39,50] "Cisplatinum" is known having antitumor activities, several

Pt chelates in this article fulfill this requirement and might be useful in therapy.

Metallacyclophosphazenes **34i,r** can be converted into phosphazene polymers with metals in the backbone with average molecular weights of ca. 24 kDa (Mo) and 34.5 kDa (W).

Group 13 (Al, Ga, In) chelates might serve as single-source precursors for the generation of III/V semiconductors.

Further studies will be directed toward the synthesis of new ligand systems and the incorporation of other metals, e.g. rare earth metals. The application of these heterocycles in material science, catalysis, and biochemistry is another challenging target for the future.

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IX. References

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