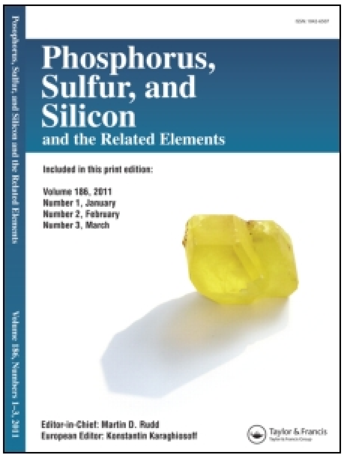

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Contributions to the Chemistry of Twofold-Coordinated Group 15/14 Element Heterocycles (A Personal Account)

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Contributions to the Chemistry of Twofold-Coordinated Group 15/14 Element Heterocycles (A Personal Account)

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Synthesis, properties, and reactivity towards metal compounds of benzo- and pyrido-anellated 1,3-azaphospholes and 1,3,2λ^2-diazaelement-2-ylidenes are described. They present heterocycles bearing a twofold-coordinated (σ^2) group15 element in 3- or a σ^2-group14 element in 2-position. Migration of substituents between the 2- and 3-position that would make them isomers was so far not observed. Nevertheless, they are relatives with respect to stabilization of the twofold-coordinated element by inclusion into a cyclodelocalized 10π-electron system and by weak donor but notable π-acceptor properties.

Keywords Catalysis; germylenes; hybrid ligands; low coordination; metal complexes; phosphorus heterocycles

INTRODUCTION

Background

The application of quantum chemical concepts to the main group chemistry had shown early that (p-p)π bonds are much less stable for higher-row than for second-row elements, and closer inspection of the literature at this time had revealed that all formulas of higher-row element compounds described in analogy to olefins, imines, or carbonyl compounds were wrong, except those of some sulfur compounds, leading

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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to the so-called classical double-bond rule.[1] This challenged researchers to find exceptions also for other main group elements. The first encouraging hints come from the detection of unstable phosphaacetylene,[2] but a breakthrough to isolable compounds of higher group15 element compounds came just a few years later with the synthesis of the first twofold-coordinated phosphorus compounds, stabilized by inclusion of σ^2-phosphorus into delocalized cationic π-systems[3] or cyclodelocalized heterocycles,[4] later also exclusively by steric bulk.[5] The pioneering work was followed by intensive research in this field, leading to many new types of P=C compounds and the recognition that the behavior of P=C compounds is usually closer to that of related C=C than of homologous C=N compounds, which expresses the diagonal relationship of carbon and phosphorus.[6] The first compounds with As=C bonds were also reported in the early phase,[7] while silicon and germanium[8] compounds with (p-p)π-bond were discovered only in the 1980s.

The idea to stabilize less stable low-coordinated compounds concerned not only higher row-elements but also two-valent carbon and inspired Wanzlick and coworkers in the early 1960s to search for isolable heterocyclic diaminocarbenes (NHC).[9] The concept was supported by early theoretical work[10] and is valid as known today, but compounds and reaction conditions were not optimal, so that only dimers were obtained and stable monomer NHCs were reported for the first time only in 1991 by Arduengo et al.[11] Diaminostannylenes[12] and diaminogermylenes[13] were known already at this time, but their stability was attributed rather to the generally increased stability of two-valent higher row group14 elements than to (p-p)π -bonds. The role of π -bonds for stabilization of monomer silylenes was shown in the later 1980s and early 1990s by theoreticians,[14] but the search for syntheses of first diaminosilylenes[15] and further work on related higher homologues was inspired by the discovery of the NHCs and later by their rapidly increasing meaning as ligands for coordination chemistry[16] and catalysis.[17]

The interest of one of us in π -stabilized twofold coordinated main-group elements dates back to the late 1970s and turned from arsenic[18] to phosphorus[19] and later also to silylenes,[20] germylenes,[21] and carbenes.[22] The major part of this work concerns benzo-, a minor part pyrido-anellated element$^{15/14}$-azoles with the structural unit E^{15}-E^{14}-N where either E^{15} or E^{14} has the coordination number two (Figure 1). In the following article, a short personal overview on these compounds is given, comprising syntheses, structural aspects, and reactivity towards metal compounds.

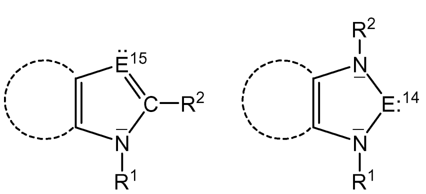
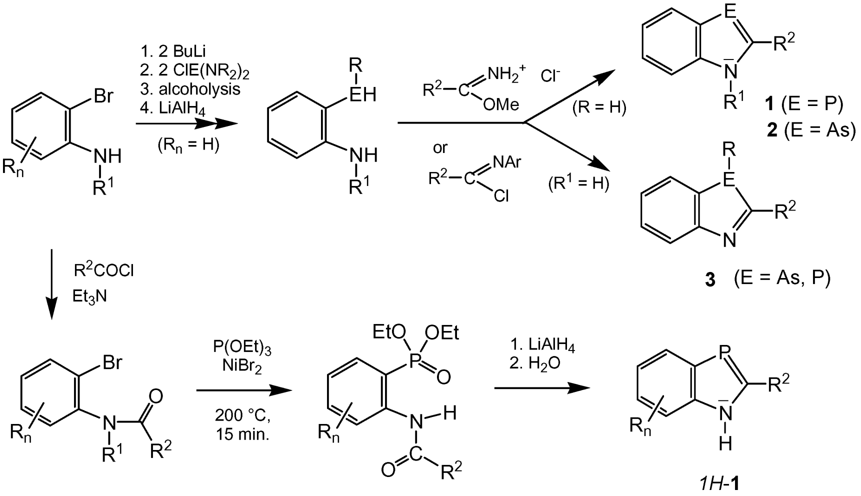


FIGURE 1 Benzo- and pyrido-anellated imidazol- and imidazol-2-ylidene-type heterocycles stabilizing twofold-coordinated higher-row group15 (P, As) and group14 elements (C, Si, Ge).

P- AND As-HOMOLOGUES OF BENZO- AND PYRIDO-ANELLATED IMIDAZOLES

Synthesis

Replacement of one nitrogen atom of benzimidazoles by a phosphorus or arsenic atom leads to either 1 *H*-isomers **1** and **2** with the double bond between the heavier element and carbon or the 3 *H*-isomers **3** with a C=N double bond and threefold-coordinated heavier atom. The heterocycles were synthesized by multistep procedures via 2-phosphino- or 2-arsinoanilines, which originally were synthesized by element-specific methods,[18a,23] later involving organometallic carbon element coupling steps.[18c,19b,24] The final cyclocondensation was achieved under mild conditions with imino carboxylic acid derivatives or orthoformates (Scheme 1).[18a,19b,25] For *N*-unsubstituted 1 *H*-1,3-benzazaphospholes

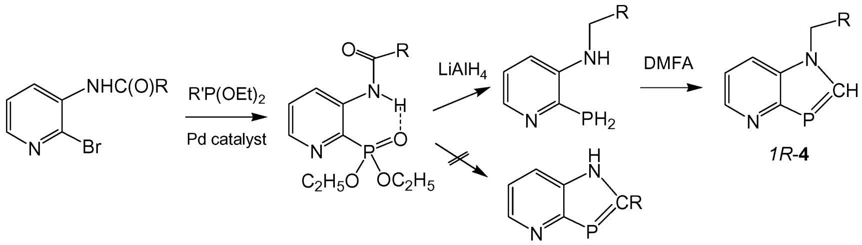


SCHEME 1 Synthesis of 1,3-benzazaphospholes and -arsoles.

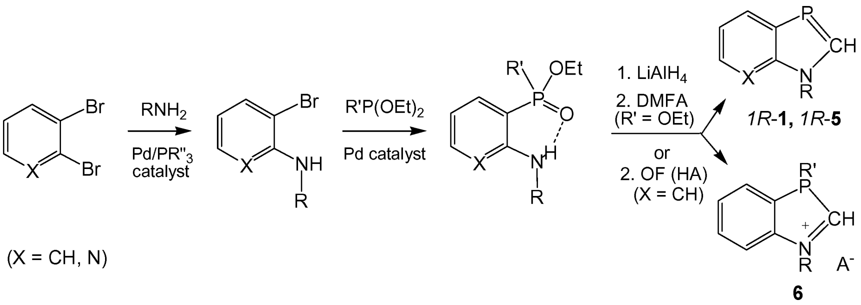
(1*H*-**1**), a convenient alternative two-step access starting from 2-bromo- or 2-chloroanilides was developed, comprising nickel-catalyzed coupling with triethylphosphite and subsequent reductive cyclization with excess $LiAlH_4$.[26]

Bulky *N*-substituted 1,3-benzazaphospholes and likewise 2-pyridyl-benzazaphospholes or pyrido-anellated 1,3-azaphospholes are not accessible by the above routes. Attempts to couple *o*-lithiopyrido-lithiumanilides with $ClP(NMe_2)_2$, $ClP(OEt)_2$, or $ClP(O)(OEt)_2$ failed to give defined products, likewise attempts of nickel-catalyzed coupling of amino- or *N*-tertiary amido-*o*-bromoanilines or -pyridines with triethylphosphite. However, palladium-catalyzed cross couplings, followed by reduction of the resulting *o*-anilino- or *o*-aminopyrido-phosphonates and condensation with dimethylformamide dimethyl acetal, led to the desired *N*-substituted benzazaphospholes 1*R*-**1**,[27] 1,3-azaphospholo [4,5-b]pyridines **4**, or 1,3-azaphospholo[5,4-b]pyridines **5**[28] (for comparison with benzanellated compounds also named pyrido-anellated azaphospholes). In these reactions, *E*-phosphaalkenes can be observed as intermediates by NMR, which gives evidence that the first step in the condensation is the reaction at the primary phosphino group. Cyclization of bulky *o*-arylaminophenyl-phosphaalkenes requires acid catalysis, which in general accelerates the cyclocondensation. Reduction of *o*-acylamidopyridinephosphonates did not lead to reductive cyclization but to reduction of the *N*-acyl group and usually low yields of the respective primary phosphines. These were then also cyclocondensed with DMFA (Schemes 2 and 3). *N,P*-Disecondary *o*-anilinophosphines are available in the same way. An 1,3-benzazaphospholium salt **6**, a potential aminophosphinocarbene precursor, was obtained by reaction with orthoformiate in the presence of an anhydrous acid.[29]

Pyrido[a]-anellated 1,3-azaphospholes, possessing a bridging N-atom, were synthesized by different routes. 1,3-Azaphospholo[1,2-a] pyridine (1-phosphaindolizine) **7** (R = $OSiMe_3$) was obtained by



SCHEME 2 Synthesis of azaphospholo[4,5-b]pyridines.

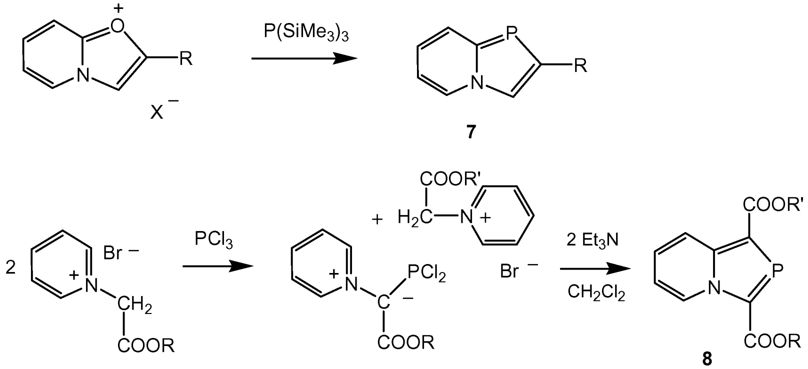


SCHEME 3 Synthesis of *N*-substituted 1,3-benzazaphospholes and azaphospholo[5,4-b]pyridines.

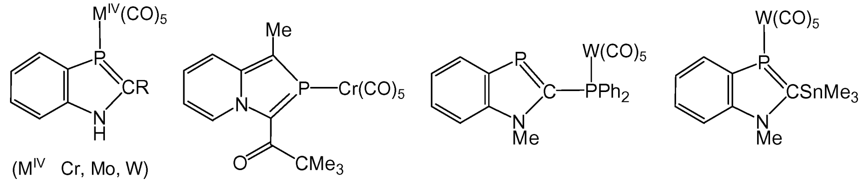
oxonium-phosphorus exchange reaction of zwitterionic 1,3-oxazolo[3,2-a]pyridinium-2-olate (R = O^-) with $P(SiMe_3)_3$,[30] while 1,3-azaphospholo[1,5-a]pyridines (2-phosphaindolizines) **8** were formed by reaction of *N*-alkylpyridinium bromides, activated by an ester or similar –M-group, with PCl_3 in the presence of Et_3N.[31] The reaction proceeds via a pyridinium dichlorophosphinomethylide that undergoes dismutation yielding **8** (Scheme 4).[32] This method was applied also to anellated pyridines and five-membered azolium salts and led to various heterocyclic anellated 1,3-azaphospholes.[31,33,34] 2-Phosphaindolizines **8** can also be obtained by reaction of pyridinium bis(ethoxycarbonyl)methylide with *tert*-butyl-phosphaethyne.[35]

Coordination Properties

The 1*H*-isomers of 1,3-benzazaphospholes and -arsoles, **1** and **2**, proved to be surprisingly thermally stable, weakly acidic instead of basic



SCHEME 4 Synthesis of 1,3-azaphospholo[1,2-a]pyridines (1-phosphaindolizines) and 1,3-azaphospholo[1,5-a]pyridines (2-phosphaindolizines).



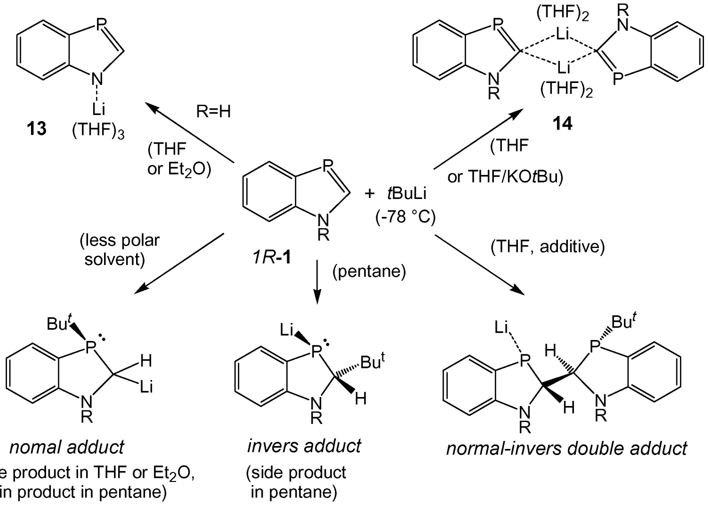
9 **10** **11** **12**

FIGURE 2 Benzazaphosphole and 2-phosphaindolizine M(CO)$_5$ complexes.

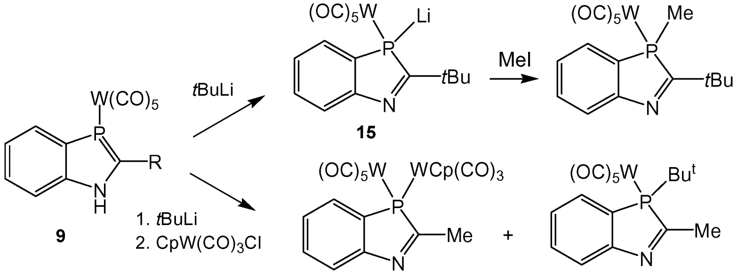
at nitrogen, and very weak σ-donors at phosphorus. While usual σ^3-phosphines easily form BH$_3$ adducts, the 1 *H*-1,3-benzazaphospholes are unable to do this. Even electron-rich transition metal compounds such as [RhCl(1,5-COD)]$_2$ or [PdCl$_2$(1,5-COD)], which form complexes with rather weak donors by cleavage of the chloro bridges or replacement of COD and are capable of π -back-bonding, did not form coordination compounds.[29] Only reactions with M^{VI}(CO)$_5$(THF) (M^{VI} = Cr, Mo, W) furnished complexes **9**, which were thermally even quite stable (Figure 2).[36] This shows that neutral benzazaphospholes must be efficient π-acceptor ligands to compensate for the weak σ-donor strength. The ^{31}P NMR spectra display very low downfield coordination shift for the chromium carbonyl complexes and up-field or even strong up-field coordination shifts in case of molybdenum or tungsten carbonyl complexes and thus confirm the π-acceptor properties. Single crystals for closer structural information on the benzazaphosphole metal penta(carbonyl) complexes could not be obtained, but this was possible for the phosphaindolizine Cr(CO)$_5$ complex **10**,[37] showing the Cr(CO)$_5$ group within the plane of the five-membered ring and the carbonyl frequencies rather hypsochromic (2071 m, 1954 s, 1940 s cm^{-1}) and indicating weak donor properties. The $\Delta\delta(^{31}P)$ value was very similar to those found for benzazaphosphole Cr(CO)$_5$ complexes.[25b,36] The preferred coordination in **11** with the P,P′-hybrid ligand 1-methyl-2-diphenylphosphino-benzazaphosphole gives evidence that coordination of W(CO)$_5$ is stronger at the σ^3-phosphino group than at the σ^2-phosphorus despite the rather strong back-bonding exhibited just by the tungsten complex **9** (M^{IV} = W). In the 2-stannylbenzazaphosphole W(CO)$_5$ complex **12**, the C—Sn bond is strongly destabilized (slow decomposition to 2-CH complex) compared to the free ligand,[38] possibly by intramolecular interactions with oxygen of an *cis*-carbonyl group. A rearrangement to an alternative stannylphosphino carbene W(CO)$_5$ complex was not observed.

Metalation and Coordination of the Anions

The 1 *H*-isomers of benzazaphospholes and -arsoles, **1** and **2**, are not only thermally stable, but compared to most other P=C or As=C species, they are unexpectedly resistant to the addition of water, even to aqueous acids and bases and in part to strong metalation agents.[18,19] This allowed lithiation of 1 *H*-**1**[25b] and 1 *H*-**2**[18c] with lithium amides. More advantageous was the use of *tert*-butyllithium that enabled lithiation of 1 *H*-**1**[39] at the nitrogen atom and of non-bulky *N*-substituted 2*H*-**1**[38] and 2*H*-**2**[18c] at CH-2 in polar solvents without amine as side product. However, if bulky *N*-substitutents hinder lithiation at CH-2, addition of *t*BuLi at the P=C bond was observed, even in the polar solvent THF. In borderline cases, e.g., R = neopentyl, addition of KO*t*Bu shifted the reaction towards CH-lithiation, while use of unpolar pentane caused the opposite, only addition. This occurred in both normal and inverse mode. With certain additives, even a normal-inverse double addition was observed (Scheme 5). The highly diastereoselective addition reactions possess a promising potential for syntheses of functionally substituted asymmetric phosphine ligands,[27c] but as the focus here is on low-coordinated phosphorus compounds, this point will not be discussed in detail. Pyrido-anellated 1,3-azaphospholes of type **5** and **6** also tolerate water and in part aqueous acids and bases, but the resistance to addition of *tert*-butyl lithium is lower and "normal" addition is the usual



SCHEME 5 Lithiation of 1 *H*- and 1 *R*-1,3-benzazaphospholes by *t*BuLi.



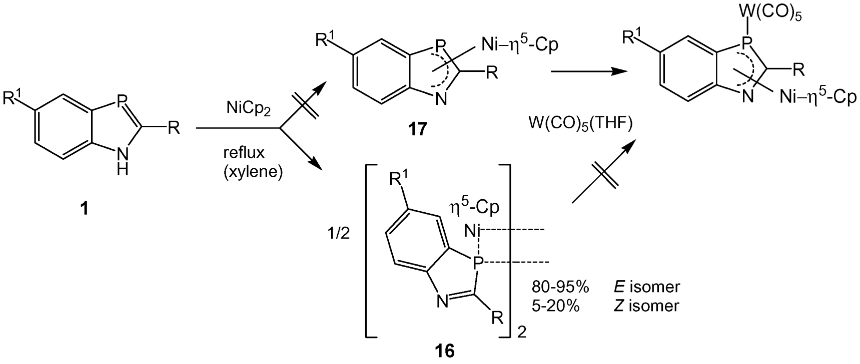
SCHEME 6 Lithiation of benzazaphosphole carbonyl complexes and electrophilic substitution.

behavior. Pyrido[a]-anellated 1,3-azaphospholes, where the nitrogen atom and its π-donor capacity is shared by the five- and six-membered ring, are even more sensitive to addition reactions.

The reactivity of 1-lithium 1,3-benzazaphospholides **13**[39] and analogous arsolides[18c] shows ambident character and coordination of soft main group or transition metals only at phosphorus, while hard electrophiles such as Ti(IV) or Zr(IV) halides did not give defined compounds. Lithiation of the NH function without addition at the P=C bond was achieved also for 1*H*-1,3-benzazaphosphole-M(CO)$_5$ complexes with *t*BuLi in THF or ether at low temperature. Alkyl and transition metal halides again prefer substitution at phosphorus (Scheme 6). The very large up-field metalation and coordination shifts of the phosphorus signal ($\Delta\delta(^{31}P)$ = –100 ppm) of **15** versus **9** suggest here a phosphide structure.[40]

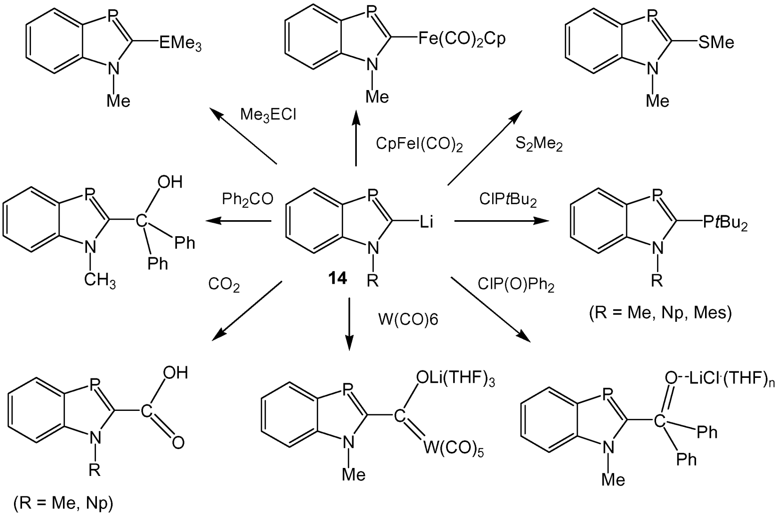
Transition metal 1,3-benzazaphospholide complexes can also be obtained directly from **1** and reactive transition metal organyls, thus by heating with nickelocene yielding dimer *P*-bridging structures **16**, which are favored to the alternative heteroallyl coordination **17**, which also should give 18 valence electron configuration (Scheme 7).[36] Carbonyl complexes could not be obtained with W(CO)$_5$(THF).

The 2-lithio reagents **14** might also be ambident as they possess lone electron pairs at phosphorus and carbon. However, all substitution reactions of **14** studied so far occurred at carbon in position 2, with hard as well as with soft electrophiles, and allowed the access of a broad variety of functionally substituted benzazaphospholes ranging from novel P,O-, P,S-, and P,P′-hybrid ligands to main group or transition metal derivatives (Scheme 8).[27,38] Even stannylation, which usually prefers the softer nucleophilic site, takes place at carbon.[38] It is supposed that the substitution in 2-position is thermodynamically more favorable by 10π-cyclodelocalization in the benzazaphosphole structure,[41]

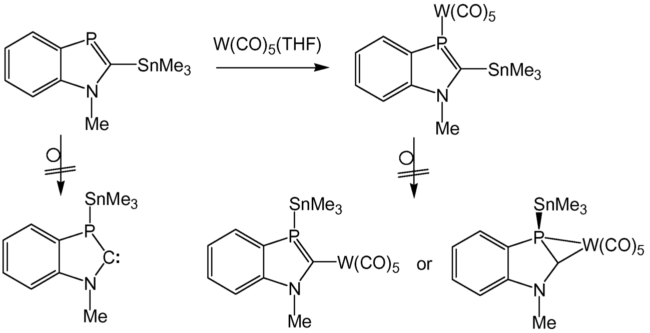


SCHEME 7 Dimer *P*-bridging benzazaphospholide nickel cyclopentadienide complexes.

which would not be possible for substitution at phosphorus (Scheme 9). In (amino)(phosphino)carbenes, the phosphorus is pyramidal, the phosphorus lone electron pair perpendicular to the formally empty p orbital of the carbene center, the P—C bond length (1.856 Å) a single bond, and the phosphino group just a spectator substituent.[42] For stannyl phosphines and phosphole type heterocycles, the barrier of inversion is strongly lowered[43] but probably not enough to allow for an alternative (stannylphosphino)(amino)carbene structure. Even the $W(CO)_5$



SCHEME 8 Reactions of 2-lithio-1-alkyl-1,3-benzazaphospholes.



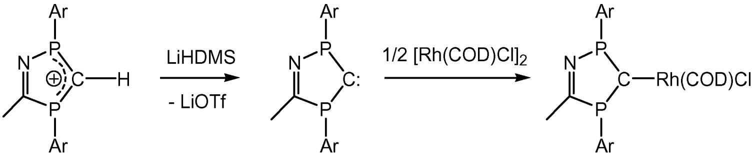
SCHEME 9 Preferred structures of a stannyl-benzazaphosphole and its $W(CO)_n$ complex.

complex preserves this structure and did not rearrange to a stannylphosphine carbene complex at ordinary conditions. The non-planar $W(CO)_4$ complex, which would represent the typical 4-electron donor properties of (phosphino)(amino)carbenes,[44] may be more stable than a planar $W(CO)_5$ complex but would require more activation energy to cleave a CO ligand.

Finally it should be mentioned that Martin et al., by extremely bulky P-aryl substituents,[45] recently could achieve the synthesis of a first cyclic unsaturated planar diphosphinocarbene, a 1,2,4-azadiphosphol-3-ylidene, and Rh-complexes thereof with usual carbene coordination (Scheme 10). This encourages us to continue the search also for mixed phosphidoaminocarbenes and their complexes.

Structures of 13 and 14

Free benzazaphospholide anions of **13** and **14** would have lone electron pairs at nitrogen and phosphorus or carbon and phosphorus, and in addition π-electrons, which for (benzo)phospholides[46] as well as pyrrolides and indolides[47] gave rise to half-sandwich complexes with alkaline metals. For solvent-free lithium 1,3-azaphospholide model molecules,



SCHEME 10 First synthesis of a diphosphinocarbene and Rh complex thereof.

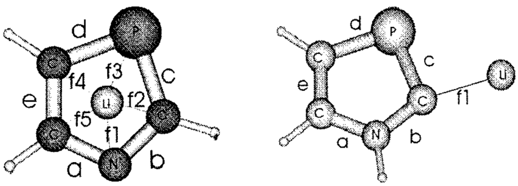


FIGURE 3 Calculated minimum energy structures (MP2/6-311++G(2d,p)) of unsolvated lithium 1,3-azaphospholides.

quantum chemical calculations revealed a half sandwich and a 2-lithio azaphosphole structure with bent C—Li bond to phosphorus as minimum energy structures for formal 1- and 2-lithiation (Figure 3).[48]

Unsolvated benzazaphospholides could not be obtained. Crystal structure analyses of lithium 2,5-dimethyl-1,3-benzazaphospholide tris(THF) solvate[39] and 2-lithio-1-methylbenzazaphosphole bis(THF) solvate (Figure 4)[38] showed lithium at nitrogen and C2, respectively, i.e., in both types, **13** and **14**, at the hard Lewis base site. However, while replacement of lithium in **13** by soft metals leads to P-coordinated complexes, products of **14** do not follow the HSAB principle but preserve coordination at C2. This means that the higher coordination strength of the carbene site as compared to the σ^2-phosphorus donor site in the anion of **14** controls the bonding position. In acyclic (phosphino)(amino)carbene complexes the situation is different, as here the lone electron of σ^3-phosphorus is not involved in P—C^{II} (p-p)π bonding and allows for additional coordination, making these carbenes to 4-electron donor ligands.[44]

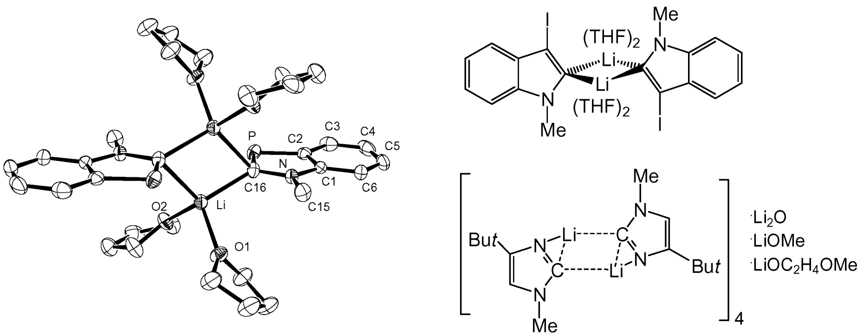
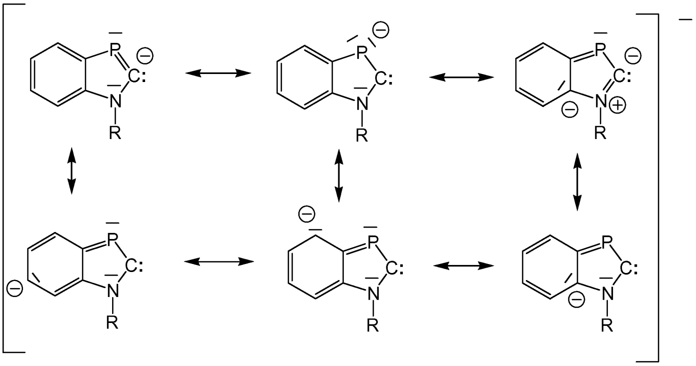


FIGURE 4 Crystal structure of 1-methyl-1,3-benzazaphosphol-2-yllithium (2 THF), and comparison with 3-iodo-1-methylindol-2-yllithium and 4-*tert*-butyl-1-methylimidazol-2-yllithium.



14

SCHEME 11 Resonance structures of 1 *R*-1,3-benzazaphospholide anion.

The description of **14** as a carbanion in analogy to 3-iodo-1-methylindol-2-yllithium[49] rather than as a phosphido-aminocarbene lithium complex in analogy to 4-*tert*-butyl-1-methyl-imidazol-2-yllithium[50] owes to the dimer μ_2-C bridging structure, which is typical for aryllithiums, while *N*-heterocyclic carbenes usually coordinate in a planar fashion,[16] also in alkaline metal complexes.[51]

For lithium and other electropositive metals, recently bent NHC-amide complexes were reported, and bending was attributed to the ionic character of the C—M bond.[52] Since the ionic bond is undirected, μ_2-NHC complexes might also be possible with alkaline metals if the negative charge at carbon is sufficient to bind two cations in this mode. In the formal anion of **14**, the σ -electron withdrawal is less than in the push–pull (benz)imidazol-2-ylidenes, because phosphorus is less electronegative than nitrogen and carbon so that such a situation may be assumed and expressed by resonance structures with a relatively high weight also of the phosphido carbene resonance structure (Scheme 11).

For the above indol-2-yl and related *N*-substituted pyrrol-2-yl anions, the situation looks not much different—instead of the lone electron pair of phosphorus there is the bonding electron pair to R3—so that similar resonance structures can be drawn, and these compounds formally can be regarded as α-carbanionic aminocarbenes. This shows that the electronic situation in aryl anions, particularly with α-nitrogen atom, is not much different from that in cyclodelocalized NHC. This is reflected by the ^{13}C NMR spectra, where the anionic C2 of **14** is found in the region $\delta = 247-250$ ppm ($\Delta\delta = 87-90$ ppm)[27,38] and thus even more downfield shifted as the carbon resonance of the two-valent carbon in the structurally related 1,3-bis(neopentyl)-benzimidazol-2-ylidene ($\delta = 231-232$ ppm).[22a,53,54] The general strong downfield shift in aryl anions, for $C_6H_5^-$ versus C_6H_6 $\Delta\delta(^{13}C) = 58$ ppm, was attributed to σ -electron/π -electron repulsion,[55] which increases considerably with increasing size of the adjacent heteroatoms ($\Delta\delta$ N < C < S < P < As) and reaches $\Delta\delta = 87-90$ ppm in **14** and $\Delta\delta = 98$ ppm in the closely related 1-methylbenzazarsol-2-yllithium ($\delta = 275$ ppm),[18c] respectively. The polarization leads to transfer of π-density into anellated rings, for **14** to up-field carbon chemicals shifts of the benzene carbon nuclei of $\Delta\delta = -4$ to -7 ppm. For anellated NHCs, slightly smaller but similar effects are observed.[22]

Si- AND Ge-HOMOLOGUES OF BENZO- AND PYRIDO-ANELLATED IMIDAZOL-2-YLIDENES

N-Heterocyclic carbenes, with flexible electropositive N-substituents such as protons, silyl, or stannyl groups etc., are unstable with respect to their isomers having these groups at C2 and forming a C=N double bond. However, if the two-valent carbon is replaced by a higher-row group14 element, then the flexible group prefers to bond at the nitrogen atom. Long-known examples are *N*-silylated heterocyclic diaminogermylenes[56] and –stannylenes.[57] For various diazasiloles, the relative energies were calculated by quantum chemical methods, which show that the silylene is the most stable isomer (Figure 5), while the gain in energy by cyclodelocalization is larger for the Si(H)=N compound.[58]

Syntheses

Attempts to synthesize trimethylsilyl-1,3,2-benzodiazasilole or the -2-ylidene isomer by reaction of lithiated *N*-alkyl-*o*-phenylenediamines with $Me_3SiSiCl_3$ have failed so far, but cyclization of dilithiated *N*,*N*′-dineopentyl-*o*-phenylenediamine with $SiCl_4$ and subsequent reduction with potassium provided the corresponding benzodiazasilol-2-ylidene **18** as distillable compound.[15c] Its reactivity was then explored extensively by Gehrhus and Lappert,[15b] including coordination chemistry. The related pyrido[b]-anellated silylene **19** could be obtained analogously (Scheme 12), but was kinetically much less stable and decomposed extensively (residual yield 4–6%) on distillation in high vacuum, while the pyrido[c]-anellated silylene **20** could not be detected at all. We therefore synthesized also the homologous germylenes **21** and **22**, which are much more easily accessible, because $GeCl_2$·dioxane can be

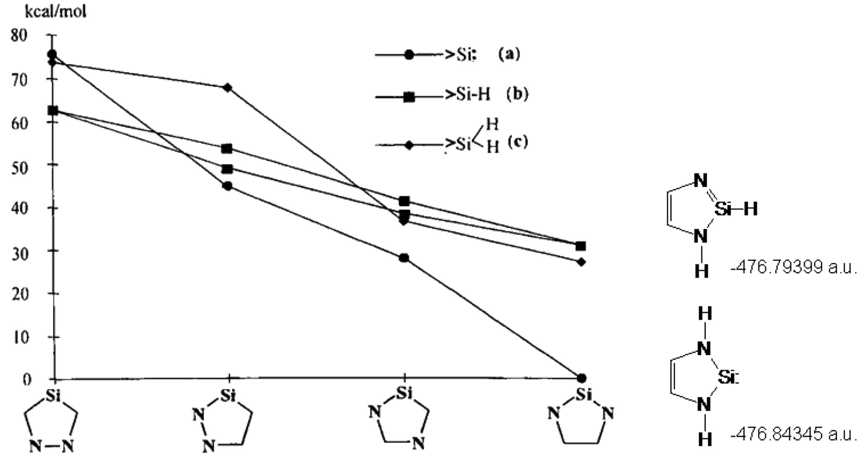
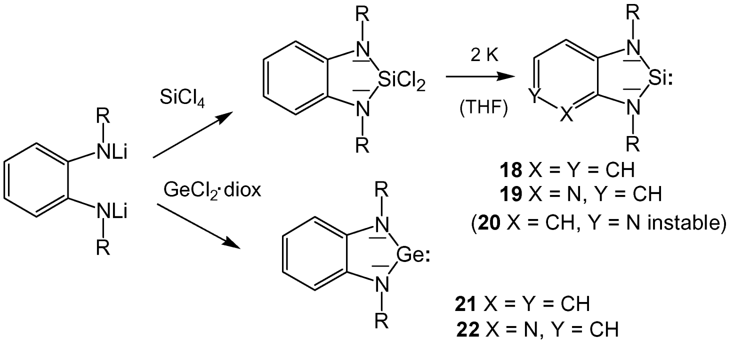


FIGURE 5 Relative energies of diazasilole isomers (using MP2/6-311G* level of theory).

used as a building block. The corresponding silylenes and germylenes display similar properties. **21** is thermally surprisingly stable, while **22** decomposed considerably during high vacuum distillation (residual yield 28% from crude 80%), and the pyrido[c]-isomer could not be obtained. Quantum chemical calculations of the silylenes showed similar thermodynamic stability of **18**–**20**, but they differ in their HOMO electron distribution, which strongly influences orbital controlled reactions. The HOMOs of all three isomers are π-states with two nodal planes. In the benzanellated silylene, the π-electron distribution is highly symmetrical, and in the pyrido[b]-compound it is similar, since a



SCHEME 12 Synthesis of anellated *N*-heterocyclic silylenes and germylenes.

nodal plane crosses the pyridine *N*-atom, but in the pyrido[c]-anellated NHGes the π-distribution is strongly asymmetrically. This lowers the activation barrier for consecutive reactions and/or decomposition and may explain the above observations.[20b] The analogous NHCs, available by deprotonation of the corresponding anellated imidazolium salts with KH in THF, are all isolable and distillable in high vacuum, as there the π-bonds are more stable, and the carbon lone electron pair becoming the reactivity controlling HOMO.[22a]

Coordination Properties

The coordination behavior of non-anellated and benzo-anellated *N*-heterocyclic silylenes (NHSis) was investigated mainly by Hill and West[15a] and Gehrhus and Lappert,[15b] respectively. Only very little work has been done concerning applications in catalysis.[59] The NHSis are much weaker σ-donors than NHCs but may act as such, e.g., to complex lanthanoide cations (η^3-Cp_3Y, η^3-Cp_3Yb, η^3-Cp_2Sm).[60] Also a Cu(I) complex, a few complexes with two-valent palladium and platinum,[61] and ruthenium(II) complexes[62] were reported, while nickel(II) of $[NiCl_2(PPh_3)_2]$ was reduced by **18** and provided $Ni(0)(PPh_3)(NHSi)_3$ and $Ni(NHSi)_4$, depending on the stoichiometry.[61] Further NHSi-coordination compounds concern complexes of zero-valent electron-rich transition metals.[15a,b] Transition metal complexes of NHGe were rarely investigated,[12] in view of their easier access. The reason might be that they are more labile. Just as for 1 *H*/*R*-1,3-benzazaphosphole ligands, only 18 VE complexes with zero-valent electron rich metals (Ni, Mo) are known,[13b,63–66] obtained, e.g., by reaction with Ni(1,5-COD)$_2$, $Mo(CO)_4(EtCN)_2$, or $Mo(CO)_3$(cht) (cycloheptatriene). Attempts to synthesize Pd(II) or Rh(I) complexes of **21** with $[AllPdCl]_2$ or $[Rh(COD)Cl]_2$ failed. This suggests that NHGe are likewise weak σ-donors and require π-back-bonding for stabilization. The reason might be the strong decrease of lone electron pair orbital energy from NHC over NHSi to NHGe (Figure 6).[65a]

Evidence for the low donor strength of NHGes was provided for octahedral *fac*-$(NHGe)_3Mo(CO)_3$ complexes with dineopentyl-diazagermol-2-ylidene and **21** as ligands (Figure 7), which are all *trans* to CO. The CO bands were found strongly hypsochromic shifted ($\bar{\nu}_{CO} = 1961$, 1853; benzo-anellated $\nu_{CO} = 1966$, 1942, $1898\ cm^{-1}$)[65] compared to those for a related bis(imidazol-2-ylidene)$Mo(CO)_4$ complex ($\nu_{CO} = 1905$, $1778\ cm^{-1}$).[67] The short Mo-Ge(II) bond lengths, which are even shorter than most Mo-Ge(IV) bonds,[68] account for stabilization by π-back-bonding. The remarkable deviation of the Mo atom out of

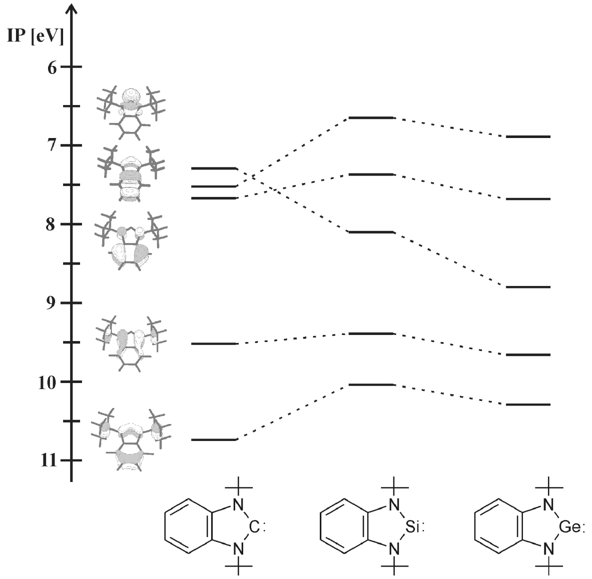


FIGURE 6 Correlation scheme of calculated ionization potentials of NHE(II) model compounds.

the average ring plane and bending within the ligand (torsion angle of N-Ge-N versus N—C—C—N plane ca. 8 degrees) is attributed to steric factors and destabilization of the ligand 10π-system by electron–electron repulsion as consequence of π-back-bonding. Similar effects

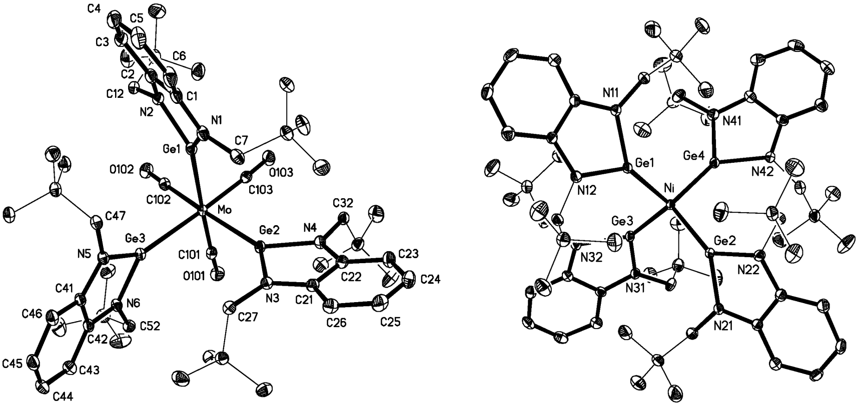


FIGURE 7 Molecular structures of *fac*-$(NHGe)_3Mo(CO)_3$ and $(NHGe)_4Ni$ with ligand **21** in the crystal.

are observed for the extremely air- and moisture-sensitive distorted tetrahedral $(NHGe)_4Ni$ complex (Figure 7) of the ligand **21**.[65a]

Because of the low π-density at Ge(II), the diaminogermylenes can also act as electrophiles, either towards strong bases such as NHC, forming bent Lewis acid–Lewis base adducts,[54,69] or by more electron-withdrawing quinoxaline anellation, which leads to coordination of chloride at Ge(II).[70] Such properties have not been observed so far in benzazaphospholes, where the higher row donor atom is in position 3 and has higher π-density by conjugation with the N-atom in the 1 position. There is so far no clear evidence that this leads to π-donor properties, but it might diminish the π-acceptor strength and be the reason that benzazaphospholes coordinate only zero-valent metals with strong π-back-bonding and in contrast to many other P=C compounds[6] are unable to bind even electron-rich d^{10} or d^8 transition metal cations.

CONCLUSIONS

While twofold-coordinated nitrogen in imines, pyridine-, or imidazole-type heterocycles and twofold-coordinated carbon in *N*-heterocyclic carbenes are strong σ-donor and usually weak π-acceptor ligands with the lone electron pairs usually being the HOMOs of the ligands, their higher homologous counterparts, here presented by benzazaphospholes and -arsoles and *N*-heterocyclic silylenes and germylenes, are weak σ-donors by energetically much lower lone electron pairs. The lower π-bonding strength and occupation of π-orbitals in NHSi and NHGe facilitates, however, back-bonding and thus favors coordination of low- or zero-valent electron rich metals. In the 1,3-benzo-elementazoles, as the π-electron density in the 3-position is higher than in the 2-position, back-bonding is less efficient and in benzazaphospholes allows coordination only of zero-valent metals, while coordination of one- or two-valent electron-rich transition metals, known for other types of P=C compounds, is unfavorable.

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