Design of Self-Adapting N-Heteroaromatic Substituted Claw Ligands as E^-/M^+ (E = P-Block Element, M = Main-Group Metal) Charge Spacers

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Monoanionic bi- and tridentate ligand systems emulating the structural features of the well-known poly(pyrazolyl)borates are created by bridging heteroaromatic rings with formally negatively charged p-block elements. Their properties and versatility are exemplified by their complexes with main group metals. Due to their N(σ)-donating and π-interacting ability, as well as the flexibility of the substituent bonding, these ligand systems have the potential to adapt both geometrically and electronically to the coordination requirements of the complexed metal. Within these complexes, the heteroaromatic substituents operate as charge spacers between the formally anionic center and the metal cation without encapsulating either site. This provides possible applications in the creation of reactive soft/hard bimetallic reagents, the realization of multinuclear arrays, and the design of preorganized CVD precursors, particularly en route to III/V-semiconducting thin films.

Introduction

A principal strategy in synthetic inorganic and organometallic chemistry is the employment of tailor-made ligand systems to create metal complexes of specific nuclearity, coordination number, geometry, and reactivity. Typical functions of such ligands are to inhibit oligomerization reactions, to stabilize the low valent form and/or the low oxidation state of the metal center, and to model the shape of the periphery of the complex. In main group chemistry, aryl and cyclopentadienyl rings are widely used examples of sterically and electronically active substituents.

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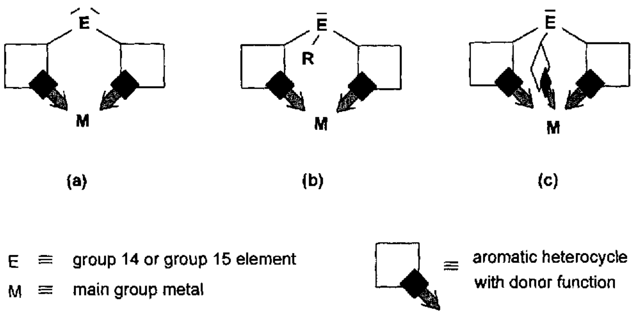
Appropriately substituted aryl ligands are able to stabilize multiple bonds between higher main group elements by combining steric shielding and electronic stabilization through their π-system.[1] The monoanionic cyclopentadienyl substituent and its derivatives are used to generate low valent cyclopentadienyl π-complexes of s- and p-block elements.[2][3] Very recently, anionic homologues of such systems have been constructed by nucleophilic addition of Cp^- to neutral metallocenes.[4]

In addition to the ability of π-interaction in homoaromatic groups, aromatic nitrogen heterocycles can σ-coordinate to a metal center through the lone pair localized at the nitrogen atom. This provides the ligand with a significantly higher flexibility since metal centers of both soft and hard Lewis acidity can be suitably complexed. Hence, it is not surprising that pyridyl and pyrazolyl groups, the isoelectronic analogues of the phenyl- and the cyclopentadienyl-substituents, adopt a key role as donor ligands in the coordination chemistry of transition metal compounds.[5] The pyridine ring constitutes an essential element in a variety of macrocyclic ligand systems.[6] Bidentate ligands such as pyridazine or monoanionic pyrazolyl and imidazolyl systems are able to form a bridge between two transition metal centers, resulting in multinuclear complexes.[5b][7] The π-system in these ligands can participate in electron transfer and magnetic coupling processes between the separated metal centers in heteronuclear and mixed valence transition metal complexes.[8] Bicyclic or macrocyclic chelate ligands with distinct steric and electronic characteristics are created when different aromatic and heteroaromatic ring systems are fused.[5a][5c][6][9] Examples of this phenomenon include spontaneous molecular self-organization, in which such macrocycles are involved in the formation of multinuclear inorganic helices.[10]

In addition to the electronic flexibility, a multifunctional chelate system should have geometric adaptability, i.e. the ligand should be variable enough to complex metal centers of different sizes. In general, this cannot be achieved by employing conjugated heteroaromatic ring systems. Instead, the single heteroaromatic rings have to be linked by a bridging group in order to allow the ring substituents to change their orientation with respect to the complex center. The poly(pyrazolyl)borates, first introduced in 1966 by Trofimenco,[11] represent well-known examples of this class of heteroaromatic substituted chelate ligands. A common feature of the pyrazolylborates is the R−B-group (R = H or an organic unit) which connects two or three pyrazolyl rings each at the 1-position. By varying the pyrazolyl ring substituents, specific properties of the corresponding metal complexes can be tuned sterically (i.e. by modification of the cone angle of the ligand) and electronically. Numerous articles reporting the successful preparation of so-called scorpionate complexes with most metals or metalloids in the periodic table demonstrate the versatility of this ligand concept.[7c][12] The tri(pyrazolyl)methane derivatives are important examples of analogous ligand systems containing bridging atoms other than boron.[12c][13] It has been shown very recently that even an aryl ring can be employed as a bridging group, providing an additional π-donor function.[13c]

Monoanionic ligands with similar characteristics can be prepared by introducing, for instance, p-block elements as bridging atoms with a formally negative charge (Figure 1). Bidentate ligands result when group 15 (a) or monosubstituted group 14 (b) elements are used to bridge two heteroaromatic rings. The bridging of three heteroaryl groups by unsubstituted group 14 elements creates monoanionic tridentate claw ligands (c).

Figure 1



The monoanionic ligand systems depicted in Figure 1 are potentially able to vary the grip of the ligand periphery by rotation of the heteroaryl rings about the central bonds, i.e. they can geometrically adapt to the size of the complexed metal center. In addition, the heteroaromatic substituents operate as charge spacers between the negatively charged bridging position and the metal cation. This provides the complex with the potential to react as both a nucleophilic and an electrophilic reagent. The electronic and steric properties of the complex can be modified by variation of the bridging atoms, the heteroaromatic substituents, and the metal center. Therefore, the preference of the complex to take part in a nucleophilic or an electrophilic reaction can be tuned.

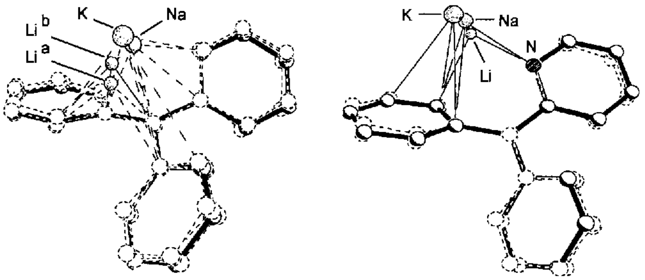
In this article we summarize our recent studies on the introduction of p-block elements as bridging groups in N-heteroaromatic substituted scorpionate-like ligand systems. The properties and versatility of these ligands have been examined by studying their complexation with main group metals.

Pyridyl-Methyl Ligands

Replacement of a single phenyl group of the triphenylmethyl carbanion by a pyridyl group has a dramatic effect on the electronic properties and the coordinative behaviour. The potential energy surface involving ions capable of delocalizing the negative charge to a maximum extent, such as in the triphenylmethyl carbanion, is often quite flat.[14] As a consequence, in the series of monomeric alkali-metalated triphenylmethane complexes ($Ph_3CM \cdot L_x$; L = donor solvent, M = Li,[15] Na,[16] K[17]) the cation shifts from the position above a $C_{ipso}-C_{central}$ bond (Li^a)[15a] to a position above the center of the anion (K) (Figure 2, left). This shift is a consequence of the decrease in the charge-polarizing effect of the metal cation. In complexes with the

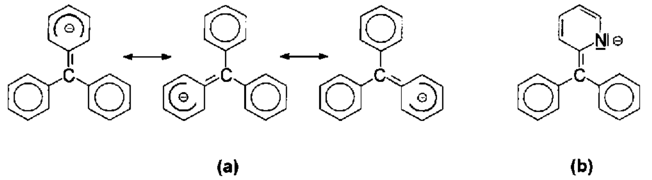
Ph_2PyC^--system (Py = pyridyl), however, the metal cation (Li, Na, K) seems to be locked in almost the same position, always preferring to coordinate to the nitrogen atom (Figure 2, right).[18]

Figure 2. Superposition of monomeric alkali metalated triphenylmethane[15][16][17] (left; Li^a and Li^b refer to structures with different donor solvents), and of alkali metalated diphenylpyridylmethane[18] (right)



The predetermined position of the alkali metal in complexes with the Ph_2PyC^- ligand can be rationalized quite well by comparing the mesomeric formulae of the anions. In alkali-metalated triphenylmethane the formulae depicted in Figure 3a become increasingly important when the size of the cation is increased. In accordance with this, the extent of the bond length variation with respect to the three central $C-C_{ipso}$ bonds drops from 4 pm to 0.9 pm on going from the lithium to the potassium derivative.[15][16][17] Furthermore, the observation that some or all cations of the polymeric potassium, rubidium and cesium analogues[19] are η^6-coordinated by phenyl-substituents is readily explained by charge delocalization over the whole anion.

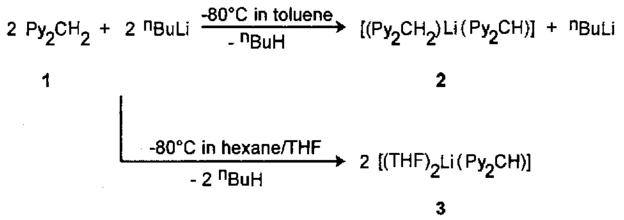
Figure 3


(a) (b)

In the pyridyl derivative, the charge delocalization over the aromatic system is distorted considerably as the negative charge is almost exclusively located at the nitrogen atom of the pyridyl substituent (Figure 3b). As a result, the C−C distance between the central carbon atom and the pyridyl ipso carbon atom is, on average, 5.5 pm shorter than the two others. This effect cannot be attributed to the difference between a C−Py and a C−Ph bond since all central $C-C_{ipso}$ bonds in the hydrogen substituted precursor $Ph_2C(H)Py$ are of equal length within their standard deviation[18] (average 152.2 pm) and do not differ from the respective $C-C_{ipso}$ bonds in Py_3CH and Ph_3CH [152(1)pm].[20]

Although the diphenylpyridylmethyl ligand only formally appears to be a carbanion, it enhances and extrapolates distinct structural features of the Ph_3C^- system and is therefore a valuable 'magnifying glass', revealing small energetic differences. An important result in terms of the design of geometrically flexible ligand systems is the observation that the environment of the central carbon atom in the pyridyl derivatives is not planar, and a small degree of rotation about the shortest $C-C_{ipso}$ bond should be possible despite its partial double bond character. This encouraged us to investigate main group metal complexes with the C−H functionalized monoanionic di(2-pyridyl)methyl ligand. The hydrogen precursor Py_2CH_2 **1**[20a][21] has already been introduced as a neutral bidentate ligand in a variety of transition metal complexes (e.g. with Hg^{2+}[22] and Cu^{2+}[23]) to tune the electronic properties of the metal center in question. The monoanionic ligand is accessible by deprotonation of **1** with strong bases like alkyllithium compounds or Grignard reagents. The metalation reaction with *n*-BuLi in hydrocarbon solvents proceeds *via* the formation of the intermediary bipyridylmethane adduct **2**[24] (Scheme 1), which can be isolated at −80 °C and structurally characterized by applying cryo-crystallographic techniques.[25] On the addition of a polar solvent, such as THF, the lithiated product $[Py_2C(H)Li{\cdot}2THF]$ (**3**) is obtained in an equimolar conversion.[24]

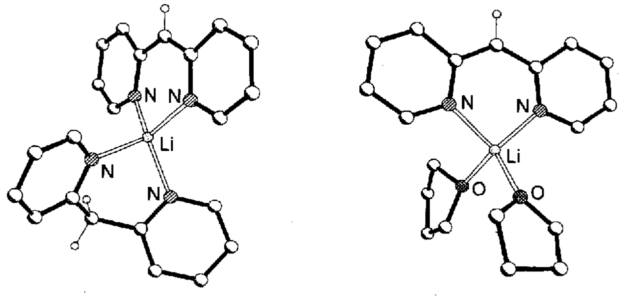
Scheme 1



The exclusive coordination in **2** and **3** of lithium by nitrogen (Figure 4) demonstrates that the anion in these complexes has to be classified as an amide rather than as a carbanion. The $Li-N_{anion}$ distances, which range from 196.0 pm to 197.6 pm, agree well with Li−N distances observed in typical lithium amides[26] while the Li−N distances to the neutral bipyridylmethane molecule in **2** are significantly longer (205.8 pm and 207.1 pm, respectively). A prerequisite for the amide-type bonding by the pyridyl groups is that the ligand system has to be completely conjugated. Indeed, the chelating anions are essentially planar (the mean deviation from the average plane through the anion skeleton is only 4 pm in **2** and 5.8 pm in **3**) and the deprotonated carbon atom is sp^2-hybridized as indicated by the geometric parameters: on average, the $C-C_{pyridyl}$ bond lengths are 140 pm and the $C_{pyridyl}-C-C_{pyridyl'}$ angles are 132° in **2** and **3**. In addition, the remaining hydrogen atom at the central carbon atom was located in the ligand plane by Difference Fourier synthesis in both structures. For comparison, the $C-C_{pyridyl}$ bond lengths and $C_{pyridyl}-C-C_{pyridyl'}$ angle for the central sp^3-hybridized carbon atom in the donating bis(2-pyridyl)methane (**3**) are 150 pm [which agrees well with a standard $C(sp^3)-C(sp^2)$ single bond of 151 pm[27]] and 115°.

The ^1H-NMR shifts can be used as another probe to illustrate the extent of electron displacement from the formally anionic center into the pyridyl rings. While the resonance signal of $H(C_{central})$ appears at almost the same position as in the neutral molecule (δ = 4.63 versus δ = 4.37 in

Figure 4. Molecular structures[24] of $[Py_2C(H)Li \cdot Py_2CH_2]$ (**2**), and $[Py_2C(H)Li \cdot 2THF]$ (**3**)

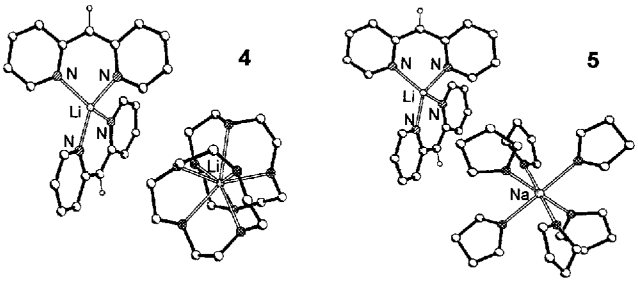


2 **3**

dipyridylmethane[21b]), the pyridyl hydrogen atoms show a significant upfield shift (δ = 5.80–7.59 versus δ = 7.07–8.58 in dipyridylmethane).

On the one hand, the complete conjugation of the anion facilitates strong bonding of the cation but, on the other hand, the flexibility of the ligand, i.e. the variability of the chelate bite, is drastically reduced by the partial double bond character between the pyridyl rings and the bridging C(H)-group. As a consequence, cations which are much larger than Li^+ should not be complexed by the bipyridylmethyl ligand. This is demonstrated by structural comparison of the respective lithium and sodium lithates. Reaction of **3** with 1 equivalent of 12-crown-4 leads to the removal of coordinating THF molecules to afford the solvent separated ion pair **4** (Figure 5, left). The anion consists of two monoanionic dipyridylmethyl ligands complexing one lithium cation in a tetrahedral arrangement. The second lithium cation, which is complexed by two crown ether molecules, constitutes the overall cation of **4**. The transmetalation reaction of **3** with NaO^tBu affords the sodium lithate **5** (Figure 5, right). Formally, the $Li(12\text{-crown-}4)_2$ cation of **4** is replaced with the $Na(THF)_6$ cation.[28]

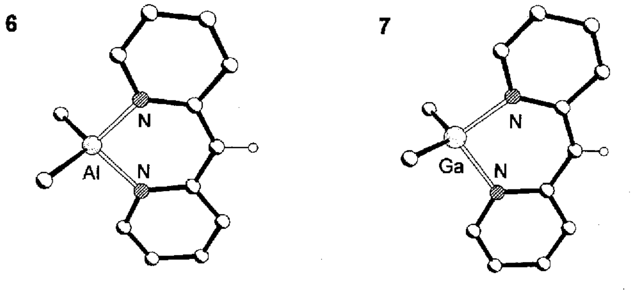
Figure 5. Molecular structures[24] of the lithates **4** and **5**



Clearly the chelate bite of the $Py_2C(H)$ anion is well adapted to the size of the lithium cation, leading to the rarely observed formation of lithates (only two lithium structures of this type were known,[29] and the sodium lithate is unprecedented). The sodium cation, however, is too large to be complexed efficiently and so total metal exchange does not occur. Within the lithate anions of **4** and **5**, the Li–N distances (average value 201.1 pm and 200.0 pm, respectively) are almost exactly halfway between the short Li–N distances in the contact ion pairs of **2** and **3** and the long L–N donor distances in **3**. The dipyridylmethyl ligand planes approach an orthogonal arrangement with respect to each other (angles between the average ligand planes are 82.3° in **4** and 88.3° in **5**). Despite the rigid bridging of the pyridyl rings by the C(H)-group, the monoanionic ligand still allows a certain flexibility as revealed by the geometric parameters in the $Py_2C(H)$-anion in **4**. The ligand framework in these systems deviates from planarity by 12.4 pm, and the pyridyl rings are twisted by 15.6° (for comparison, the twisting angles in the other anions are between 3.0° and 7.6°). However, the extent of flexibility is apparently not sufficient to cause the rather unfavorable $Na(THF)_6$ arrangement to disassemble.

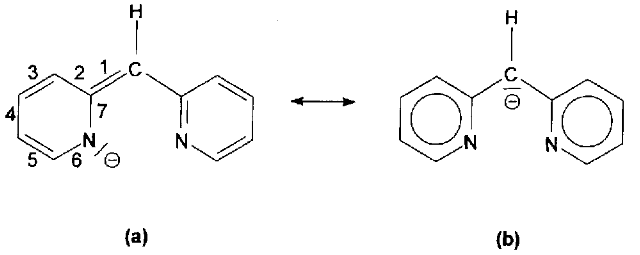
As predicted, the replacement of lithium in **2** with main group metals of similar cation size yields the corresponding chelate complexes. The dimethylaluminum (**6**) and the dimethylgallium (**7**) analogues (Figure 6) can be synthesized by a transmetalation reaction of **2** with the corresponding metal chlorides or by deprotonation of **1** with Me_3Al and Me_3Ga, respectively.[24] Compound **6** adopts an unusual monomeric structure in the solid state.[30] The extent of π-conjugation within the $Py_2C(H)$ anions is almost at maximum (0.8 pm deviation from planarity and a 0.8° ring twist angle of the pyridyl groups), hence the aluminum cation seems to have the optimum size for complexation by the $Py_2C(H)$ ligand. In agreement with this, the Al–N bond lengths (190.8 and 190.9 pm) correspond well with literature values[30b], and the Al–C distances (195.3 and 195.9 pm) are comparable with those in Me_3Al,[31] i.e. they are not influenced by the complexing ligand. The gallium structure **7** shows a close relationship to the lithium structure **2** with respect to the Ga–N distances as well as to the conformation of the chelate ligands, and this reflects the similar cation size of gallium and lithium.

Figure 6. Molecular structures[24] of the dimethylaluminum **6** and the dimethylgallium complex **7** of the dipyridylmethyl anion

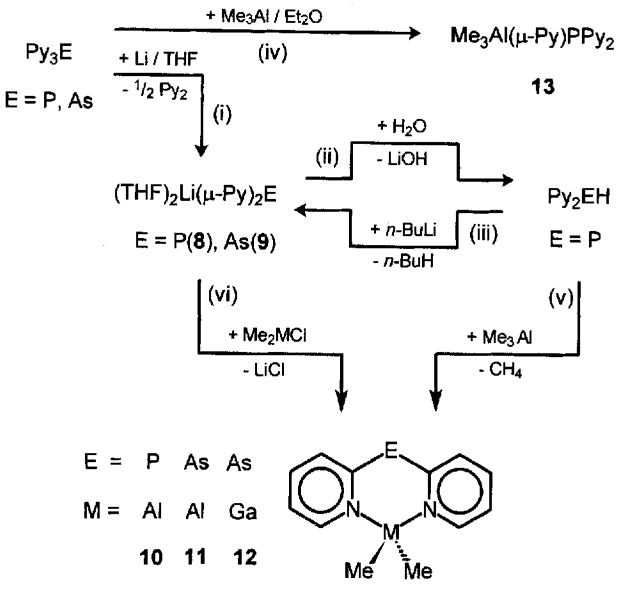


Comparison of the bond lengths in the structures **1**–**7** illustrates the presence of partially localized double bonds in the monoanionic ligand system (positions 1, 3 and 5 in Figure 7a). This prevents the chelate bite from adapting to the size of the metal cation. Thus, the $Py_2C(H)$ ligand is comparable to other chelating amides such as $Me_2Si(N^tBu)_2^{2-}$,[32] $PhC(NSiMe_3)_2^-$,[33] $RS(NR)_2^-$,[29b][34] and $Ph_2P(NSiMe_3)_2^-$.[28c]

Figure 7



Scheme 2



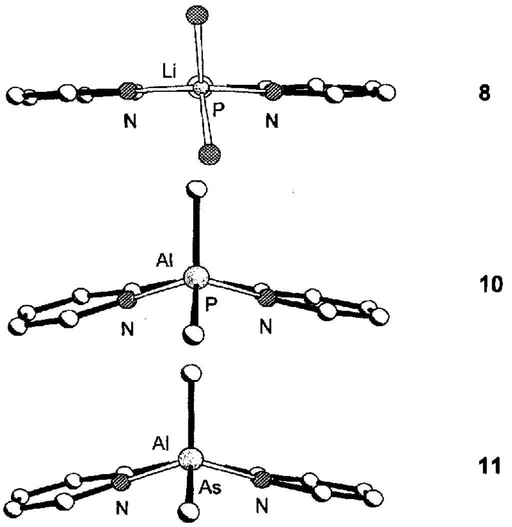
Pyridyl Phosphides and -Arsenides

The isoelectronic replacement of the C(H) bridging group in the pyridylmethyl anions by groups of lower π-acceptor/donor capabilities is one option to increase the geometric flexibility of the complexing ligand system. The heavier group 15 elements with a formally negative charge meet this criterion due to the ylide-character of the respective element–carbon bonds. In addition, these elements are of great interest as precursors for III/V semiconductors when integrated in low molecular aggregates with group 13 elements.[35] Usually, monomeric group 13/15 compounds are obtained only when extremely bulky substituents are used to protect the low valence metal center against nucleophilic attack.[36] In analogy to the bipyridylmethyl compounds, group 13 metal cations in complexes with bipyridyl phosphides and arsenides should be well separated from the formally anionic group 15 element and be exclusively coordinated by the nitrogen atoms of the pyridyl groups.

Synthetic routes to the group 13 bipyridyl phosphides and arsenides are summarized in Scheme 2.[37] Reaction of the trisubstituted pyridylphosphines and arsines with lithium metal in THF yields the lithium precursors [Py$_2$ELi·2THF] (**8**: E = P; **9**: E = As) and bipyridyl, which forms by a ligand coupling reaction of the initial product, 2-pyridyllithium, with Py$_3$E. The group 13 derivatives Me$_2$MPy$_2$E (**10**: M = Al, E = P; **11**: M = Al, E = As; **12**: M = Ga, E = As) can be prepared either by transmetalation of LiPy$_2$E with group 13 dimethylchlorides (**10**–**12**) or by metalation of Py$_2$EH (from the hydrolysis of LiPy$_2$E) with the corresponding trimethylated group 13 derivatives (**10**). In contrast to analogous reactions with organolithium compounds, treatment of tris(2-pyridyl)phosphine with trimethylaluminum yields the adduct complex **13**. The saturated coordination sphere of the aluminum atom and the strong Al–C bonds in **13** presumably prevent methyl transfer to the phosphorus atom.

The structures of the complexes **8** and **10**–**12** were investigated.[37] In each case, a monomeric compound similar to the corresponding C(H) analogue is formed. Only the pyridyl nitrogen atoms of the Py$_2$E ligand coordinate to the metal center, leaving the bridging group 15 atom separated from the cation. The structure of the lithium precursor **8** is almost exactly the same as that of [Py$_2$C(H)Li·2THF] (**3**). Geometric differences are apparent in terms of the ligand when comparing the group 13 metal complexes. While the analogous C(H) ligand system remains coplanar, the corresponding group 15 derivatives of aluminum reveal a distinct deviation from planarity in the anion. Figure 8 illustrates these deviations in contrast to the lithium complex **8**. In **10** and isotypic **11**, the pyridyl ring planes intersect at an angle of 155°. The bridging angle C–E–C′ becomes more acute: 110.4(2)° in **8**, 106.6(1)° in **10**, and, as a consequence of the increased p-character in the C–As bonds, 103.0(3)° in **11**. In addition, the intramolecular N···N′ distance (the "bite") of the ligand differs in both phosphorus compounds (**8**: 306.4 pm; **10**: 292.2 pm).

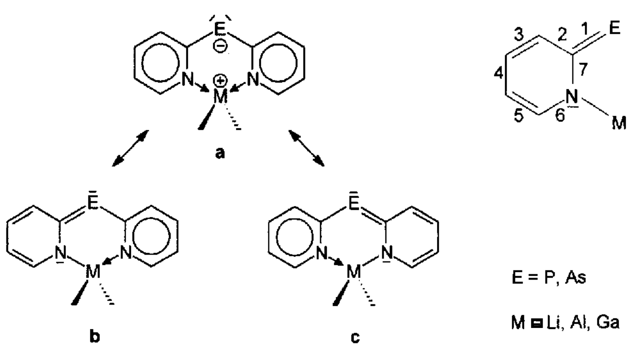
Figure 8. View along the axis through the bridging group 15 element and the metal cation in the molecular structures[37] of **8**, **10**, and **11**



On the other hand, the two E–C bond lengths are both equal, within the standard deviation, in all of the anions with a bond order between a single and a double bond (av. P–C = 179 pm vs. 185 pm for a single bond and 161 to

171 pm for a double bond in phosphaalkenes[38] ; av. As−C = 190 pm vs. 198 pm in diphenylarsenides[39] and 182 pm in arsaalkenes[40]). Moreover, the pyridyl rings have alternating bond lengths, indicating partial double bond localization in the 3- and 5-positions, as well as the accumulation of the negative charge on the nitrogen atoms (Figure 9).

Figure 9



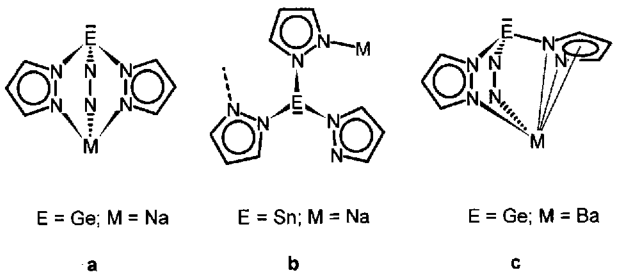
Although an X-ray structure analysis of the gallium complex $Py_2AsGaMe_2$ (**12**) could not be obtained, a geometry identical to that of **11** can be deduced from its very similar spectroscopic properties. Compared to the starting material Py_3As, the energetically highest pyridyl ring deformation vibration in the IR spectrum of **11** and **12** is shifted to higher wave numbers by coordination to the metal centers [$\tilde{\nu}$ = 1570 ($AsPy_3$),[41] 1600 (**11**), 1595 (**12**) cm^{-1}]. Metal coordination also causes an upfield shift of the 6-H signal in the ^1H-NMR spectrum of more than 1 ppm [δ = 8.67 (Py_3As), 7.61 (**11**), 7.49 (**12**)]. Hence, the monoanionic ligands of the heavier group 15 elements show a certain coordination flexibility toward different metal centers without losing full conjugation. However, the bent conformation of the anion is not static, as verified by the ^1H- and ^{13}C-NMR spectra. Despite the nonequivalence of both (M)methyl groups in the solid state, only a single signal is detected in solution even at low temperature (−80 °C). Nevertheless, coordination of the mixed group 13/15 complexes **10**−**12** to soft d-block metal centers might provide a route to hard/soft bimetallic reagents due to coordination site selectivity.

Pyrazolyl Germanates and -Stannates

A different route to monoanionic N-heteroaromatic substituted ligand systems featuring an increased geometric flexibility is the bridging of three heteroaromatic rings rather than two by suitable bridging groups. As emphasized earlier, the poly(pyrazol-1-yl)borates represent the best known examples among this class of ligand system.[11][12] In the corresponding metal complexes the central cation is effectively shielded on one side by the tripodal ligand while being open for nucleophilic attack on the other side. Different bridging groups have to be employed to provide a complex with the ability to attract electrophiles. We chose Ge(II) and Sn(II) to replace the B(H) unit in the scorpionate ligand system because the known amphoteric properties of Ge(II) and Sn(II) compounds[32][42] promise an even greater variability in the coordination behaviour. The anionic group 14 metal centers can interact with electrophiles because of their lone pair, and also with nucleophiles which saturate their coordination sphere.

Depending on the size and acidity of the cation, several coordination modes are conceivable in metal complexes with the monoanionic tripodal poly(pyrazolyl)germanium(II) and -tin(II) ligand systems $E(Pz)_3M$ (E = Ge, Sn, Pz = pyrazol-1-yl, M = main-group metal). The three arrangements observed are illustrated in Figure 10; coordination to the bridging group 14 element has never been ascertained. A tridentate (**a**) or a monodentate (**b**) coordination mode is the consequence of an exclusive N(σ) donation of the pyrazolyl ring nitrogen atoms to the metal center. A combination of the N(σ) donating capacity and the π-interacting potential of the heteroaromatic rings results in the coordination mode depicted in **c** (Figure 10).

Figure 10

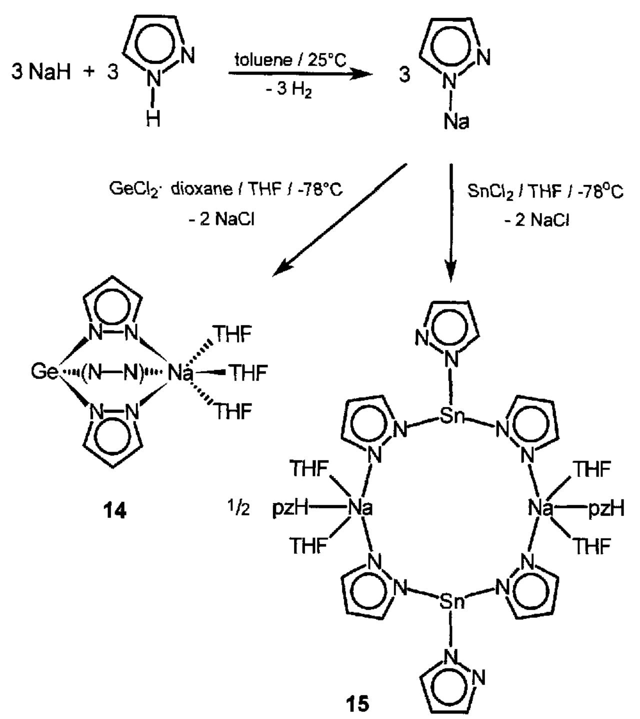


In all types of bonding, rotation of the N-heteroaromatic substituents about the E−N bond should be quite facile, permitting a high variability with respect to the grip of the monoanionic ligand. In related ligand systems like $[(^tBuO)_3E]^-$ (E = Ge, Sn, Pb)[42a][42c] and $\{[Ph(^tBu)C{=}N]_3E\}^-$ (E = Sn, Pb)[43] the rotation about the E−O or E−N bond does not influence the grip. One important aspect of our studies was therefore to compare the coordination mode in complexes of main group metals with different cation sizes and basicities.

Complexes of the tripodal monoanionic ligands $E(Pz)_3^-$ (E = Ge, Sn; Pz = pyrazol-1-yl) are accessible by the reaction of E^{II}-halides with an excess of metal pyrazolyl derivatives, such as alkali metal or alkaline earth metal pyrazolyl compounds. The resulting $E^{II}(Pz)_2$ unit interacts with unreacted $M^I(Pz)$ or $M^{II}(Pz)_2$ species to form an acid−base adduct (Scheme 3).[44] When pyrazolylsodium is used, the resulting sodium tri(pyrazolyl)germanate **14** is a monomeric complex corresponding to type (**a**), while the sodium tri(pyrazolyl)stannate **15** forms dimeric type (**b**)-like aggregates in the solid state.

The monoanionic ligands $E(Pz)_3^-$ complex the hard Lewis acid Na^+ by coordination to the hard 2-nitrogen atoms of the pyrazolyl rings. Germanium and tin are not involved in metal coordination (Scheme 3). The pyrazolyl ligands in the contact ion pairs of **14** and **15** separate the positive charge on sodium from the formally negative

Scheme 3



charge on germanium and tin. A different situation is crucial in $[Li(12\text{-}crown\text{-}4)_2][Ge(SiMe_3)_3]$.[45] In this case, the alkali metal is solvent separated from the negatively charged group 14 atom. Due to the crystallographic symmetry, all Ge–N distances [196.5(6)pm] and N–Ge–N' angles [96.2(3)°] are equal in **14**, and the structural pattern is similar to those found in tridentate tri(pyrazolyl)borate ligand systems.[12] The dimeric structure of **15** can be interpreted as a twelve-membered ring system composed of alternating sodium and tin atoms which are connected by pyrazolyl substituents.

The orientation of the pyrazolyl substituents in the $[Sn(Pz)_3]^-$ unit may give an insight as to why a tridentate coordination mode, as in **14**, is not observed in **15**. As illustrated in Figure 11, the pyrazolyl rings are arranged perpendicular to each other, with the nitrogen atoms facing outward from the ligand cone. Given the pyramidal environment of tin, this seems to be the conformation providing the least steric strain, particularly with respect to the free electron pairs at the nitrogen atoms in the 2-positions. Although the average Sn–N distance of 217 pm (which is about 20 pm longer than the corresponding Ge–N distance in **14**) creates a larger pocket to host the sodium cation, per se, this effect is outweighed by the significantly smaller bridging angle at tin (87.4° vs. 96.2° for N–Ge–N' in **14**). Apparently, the cavity in the type (**a**) form of $[Sn(Pz)3]^-$ is too small to accommodate a sodium cation on condition of appropriate Na–N distances. As derived from both structures, the Na–N distances seem to be quite restricted (244 and 243 pm in **14** and **15**, respectively).

In order to further study the different space restrictions in the tripodal type (**a**) pyrazolyl germanates and -stannates the 'homobimetallic' cations $[E(Pz^*)_3E]^+$ [Pz* = 3,5-dimethylpyrazol-1-yl; E = Ge (**16**), Sn (**17**)] containing ECl_3^- as counterions were synthesized and their structures characterized.[44b] Pz* rather than Pz was used to sterically hinder an orientation of the heteroaromatic substituents corresponding to the type (**b**) mode as observed in **15**.

Figure 11. Arrangement of the pyrazolyl substituents in **15**[44]

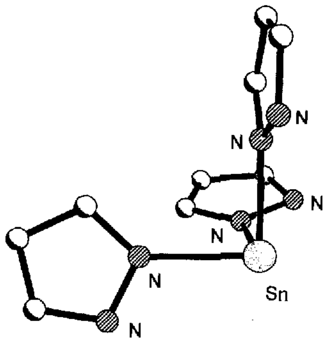
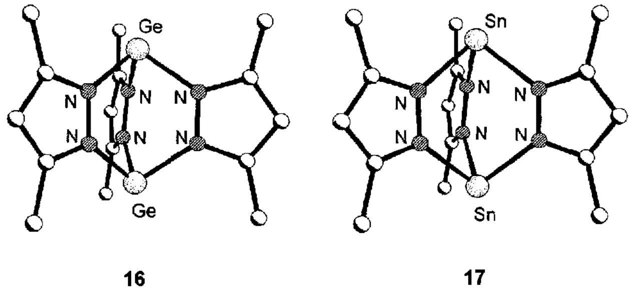


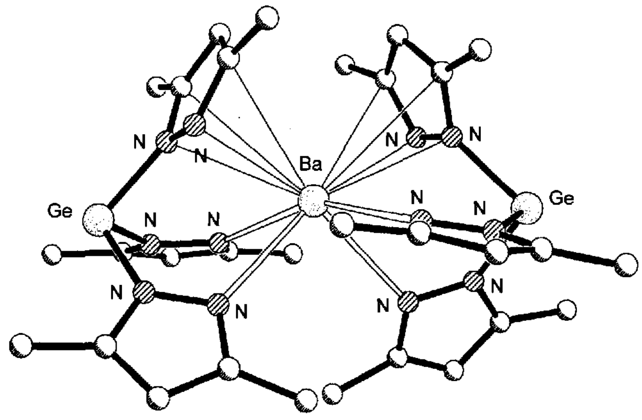
Figure 12. Structures[44b] of the cations in **16** (left) and **17** (right)



The very similar structures of the cations of **16** and **17** can be described as 'paddle-wheels' with a Ge(II) or Sn(II) shaft. The two E(II) centers are bridged *exo*-bidentate by three Pz* substituents in such a way that dicapped trigonal prisms result. The average E–N distances (E = Ge: 197; Sn: 220 pm) agree with the E–N distances in the related sodium complexes. A notable effect, however, concerns the N–E–N' bridging angles. Whereas this angle varies by only about 1° in the tin compounds **15** and **17**, a remarkable difference of 6° is observed in the germanium analogues. Hence, the bridging angle at germanium is flexible enough to allow a tripodal ligation of sodium in **14**. With the analogous tin anion this angle is quite rigid, and an 'open' arrangement of the pyrazolyl substituents with respect to the sodium cation results in **15**.

The flexibility of the monoanionic $Ge(Pz^*)_3$ ligand, in particular, can be utilized to complex bivalent cations which are far larger than the sodium cation. $Ba[Ge(Pz^*)_3]_2$ (**18**) is formed by the reaction of $Ba(Pz^*)_2$ with germanium dichloride in a 3:2 molar ratio.[44b] The reaction of $Ba(Pz^*)_2$ with $GeCl_2$ or $SnCl_2$ in a 1:2 molar ratio yields the 'homobimetallic' complexes **16** and **17**. The molecular structure of **18** is monomeric in the solid state (Figure 13). Two $Ge(Pz^*)_3^-$ ligands envelop the central barium cation in such a way that a homoleptic complex is formed. The coordination sphere of barium consists of four σ-donating nitrogen atoms and two π-interacting Pz* substituents, to resemble the type (**c**) coordination mode. To our knowledge, **18** is the first example of *side-on* coordination by a pyrazolyl ligand to an alkaline earth metal, and this demonstrates the versatility of the $E(Pz^*)_3^-$ ligand system. In the electronically isovalent poly(pyrazolyl)borate complex $Ba[BH(Pz^*)_3]$ all six nitrogen atoms coordinate exclusively with the metal center in an N(σ) manner, and an S_6-symmetry of the complex results.[46] Due to the accumulation of the negative charge at the nitrogen atoms, however, the π-coordination by the two pyrazolyl substituents is not symmetrical as it is, for instance, in cyclopentadienyl systems. While the Ba−N *side-on* distances are not much longer than the Ba−N(σ) bonds (294 vs. 280 pm on average), the $Ba-C(CH_3)$ contacts are significantly weaker [$Ba-C(CH_3)$ distances range from 328 to 339 pm].

Figure 13. Molecular structure[44b] of $Ba[Ge(Pz^*)_3]_2$ **18**



The structures of the germanium complexes **14**, **16**, and **18** prove that the size of the concave side of the ligand is tunable to accommodate a wide range of cation sizes. In addition, the ligand is able to adapt to the electronic requirements of the complex center, i.e. coordinate to both soft and hard Lewis acids. This combination provides a remarkably high coordination flexibility with the potential to create low aggregated complexes hosting almost any kind of metal cation. In particular, the monoanionic $Ge(Pz)_3^-$ ligand is a very promising candidate to design hard/soft bimetallic reagents in complexes with soft acid d-block metal centers.

Conclusion

Monoanionic ligand systems emulating the structural features of the well-known poly(pyrazolyl)borates have been designed by bridging heteroaromatic rings with formally negatively charged group 14 and group 15 elements. Their complexes with main group metals are best described as Lewis acid−base adducts. The coordination of the complex center is generally accomplished by N(σ)-interactions with the heteroaromatic substituents and always leaves the anionic center at the bridging position separated from the metal cation. The extent to which the complete anion is conjugated is one important factor which determines the geometric flexibility of the bidentate ligand systems. Due to the high tendency of carbon to form multiple bonds, the monoanionic bipyridylmethyl ligand is essentially planar, and the chelate bite is basically invariable. Isoelectronic replacement of the C(H) bridging group with heavier group 15 elements disturbs the π-conjugation and a nonplanar geometry of the ligand system results which is most pronounced in the corresponding arsenic complex. Monoanionic tridentate ligands were investigated which incorporate heavier group 14 elements as the bridging function between three pyrazolyl substituents. The germanium-bridged ligand system combines the ability to geometrically and electronically adapt to the needs of the coordinated metal cation. Examples of this include the complexation of the small sodium cation and the formation of the barium complex $Ba[Ge(Pz^*)_3]_2$ where both the N(σ)-donating and the π-interacting coordination modes are realized. Hence, this ligand system is a prime candidate to host both hard and soft Lewis acids in a suitable fashion.

In all the complexes discussed here the heteroaromatic substituents operate as charge spacers between the formally anionic center and the metal cation without encapsulating either site. This allows the complexes to react as nucleophiles due to the presence of the lone pair at the bridging element, or as Lewis acids through the cation. As an application for these systems, soft/hard bimetallic reagents with specific characteristics can be designed by introducing d-block metals as complex centers. Multinuclear linear arrays are created when soft main group elements in the bridging position connect two complex units by pπ-dπ interactions. A different possibility lies in their application in CVD processes. As the ligand systems are composed of volatile but stable substituents the monomeric binuclear complexes may prove to be valuable precursors, particularly en route to III/V-semiconducting thin films.

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