Group-13 Metal-Induced Coordination Variation of the Bis(2-pyridyl)amide Ligand in Solution and in the Solid State

Heinz Gornitzka and Dietmar Stalke*

Institut für Anorganische Chemie der Universität Würzburg,
Am Hubland, D-97074 Würzburg, Germany
E-mail: dstalke@chemie.uni-wuerzburg.de

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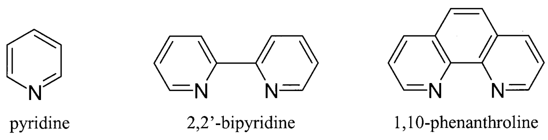
Ligands containing aromatic nitrogen heterocycles play a leading role in the molecular self assembling processes that lead to macromolecular architectures. The inductive effect of various metal fragments on those building blocks has not yet been studied systematically. To evaluate this effect we synthesized the homologous series of Group-13 metal complexes [Me_2AlPy_2N] (**1**), [Me_2GaPy_2N] (**2**), [Me_2InNPy_2]$_2$ (**3**), and [Me_2TlNPy_2]$_\infty$ (**4**) (Py = 2-NC_5H_4), and characterized them by low-temperature X-ray structure analysis and ^{15}N-NMR spectroscopy in solution. The electronic equivalence of the central and the ring nitrogen atoms leaves the energetic hyperface of the anion quite flat, and the electron density is polarized according to the requirements of the metal. In the aluminum and the gallium complexes **1** and **2** the metal center is coordinated exclusively through the nitrogen atoms within the pyridyl rings. The complexes with these hard metals are close-contact ion pairs. In the indium complex **3** the *cis-cis* orientation gives rise to a dimeric structure, while the unprecedented *cis-trans* arrangement in the thallium compound **4** leads to a polymeric structure. The complexes **3** and **4** have to be regarded as separated ion pairs of Me_2M^+ cations and Py_2N^- anions without any covalent bonds between the anionic moiety and the dimethylmetal cations, even in the solid state. The series of complexes proves the bis(2-pyridyl)amide to be an excellent self-adapting ligand. These findings are substantiated by NMR-spectroscopic studies in solution. Not only do the steric requirements of N heteroaromatic ligands have to be considered in molecular self-assembling processes but also the inductive effect of the different metal fragments.

Introduction

The use of aromatic nitrogen heterocycles has given a great impetus to metal coordination chemistry.[1] Due to the low-energy π* orbitals pyridine and its derivatives are valuable σ donors and π acceptors in the bonding synergism of transition-metal complexes.[2] Classical N-heteroaromatic donor ligands are pyridine, 2,2′-bipyridine and 1,10-phenanthroline.

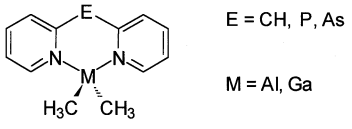
Scheme 1



In metal-induced molecular recognition processes various linkages of the simple building blocks yield polydentate macromolecular ligands tailored to the steric requirements of the nanomolecular architectures present. Helical arrangements with transition-metal centers are one focus of interest.[3] A spheric palladium polymacrocycle containing triazine bridgeheads has also been synthesized,[4] and metallo carotenate molecular wires containing pyridyl or bipyridyl ends coordinated to metal centers combine the electronic or photochemical properties of a metal fragment and the conjugated electron system of the carotenes.[5]

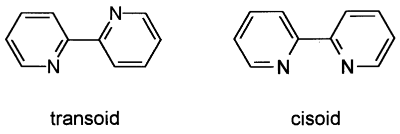
Over the last years our work has been concerned with the design and fine tuning of monoanionic ligands, containing N-heteroaromatic rings, which show a different coordination behavior towards soft and hard metals.[6] In these systems a single p block element in a low oxidation state links two or three pyridyl (Py) or pyrazolyl (Pz) rings. Metal coordination is achieved by the ring nitrogen atoms but never by the bridgehead atom. Anionic systems studied so far are the pyridyldiphenylmethyl,[7] dipyridylmethyl,[8] dipyridylphosphide and -arsenide,[9] tripyrazolylgermanate and -stannate.[10] These ligands are formally carbanions, phosphides and arsenides but in metal coordination they behave as amides. For instance the phosphorus or arsenic(III) center is only two-coordinate to both *ipso*-carbon atoms and the structures do not comprise any short M−P or M−As bonds. The negative charge in the anions is located almost entirely on the nitrogen atoms of the pyridyl substituents.

Scheme 2. Dipyridylmethyl, -phosphide and -arsenide coodination to metal centers



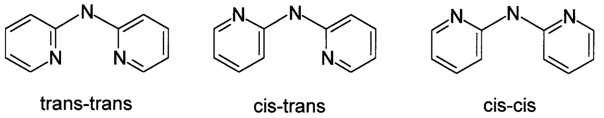
To counterbalance the electron-withdrawing effect of the ring nitrogen atoms we isoelectronically replaced the CH group, the P or the As bridgeheads by a nitrogen atom. In this paper a systematic study of the coordination behavior of the Py_2N^- anion, in both the solid state and solution, towards Group-13 metals is presented. The relationship between the geometry of a coordinated and an uncoordinated ligand system in solution and in the solid state is of special interest in the study of self-assembling systems.[11] The dipyridylamide ligand is anticipated to permit a *transoid* orientation in the uncoordinated form in solution, as found in 2,2′-bypiridine[12] and shown in Scheme 3.

Scheme 3. The *transoid* versus *cisoid* coordination of 2,2′-bipyridine



Because of electrostatic repulsion between the N lone pairs and the weak attraction between N and CH sites in antiparallel orientation of the N sites, they should favor the *transoid* over *cisoid* arrangement. A priori one can think of three different coordination modes.

Scheme 4. Feasible coordination modes of the dipyridylamide ligand



In the known complexes of neutral bis(2-pyridyl)amine the *trans-trans* coordination mode to both ring nitrogen atoms is observed [$(HNPy_2)CuHal_2$ (Hal = Br[13a], Cl[13b])], $[(HNPy_2)_2Cd{-}(ONO)_2]$[13c], $(HNPy_2)M(CO)_4$ (M = Cr, Mo, W)].[13d] In the monomeric $M(Py_2N)_2$ (M = Cu[14a], Ru, Pd[14b][14c]) complexes *trans-trans* arrangements of both ring nitrogen atoms coordinated to the metal center are found, while in $(Py_2N)W(CO)_5$,[15] the tungsten atom apparently is exclusively coordinated to the central nitrogen atom. A *cis-cis* arrangement and coordination to all three nitrogen atoms is found in the dimer of $[(Py_2N)Tl(C_6F_5)_2]_2$.[16] This coordination is emulated in the polymeric complexes of $[Cu(Py_2N)]_n$[17], $[M_3(Py_2N)_4Hal_2]_n$ (M = Cu[18a], Ni[18b]). It seems worthy to note that until now a *cis-trans* coordination of the dipyridylamide ligand has not been observed.

To study the coordination behavior of the bis(2-pyridyl)-amide anion systematically in both the solid state and in solution the Group-13 metal complexes $[Me_2AlPy_2N]$ (**1**), $[Me_2GaPy_2N]$ (**2**), $[Me_2InNPy_2]_2$ (**3**), and $[Me_2TlNPy_2]_\infty$ (**4**) have been synthesized and characterized by low-temperature X-ray structures as well as by ^{15}N-NMR spectroscopy in solution.

Results and Discussion

Preparation of 1−4

Compounds **1**−**3** were synthesized by adding trimethylmetal compounds to a solution of bis(2-pyridyl)amine (eq 1).

$$n\,HNPy_2 + n\,Me_3M \longrightarrow [Me_2MPy_2N]_n + n\,MeH \qquad (1)$$

1: M = Al; –10 °C in diethyl ether; $n = 1$

2: M = Ga; –78 °C in toluene; $n = 1$

3: M = In; 1 h reflux in toluene; $n = 2$

To obtain the compound **4** trimethylthallium has to be synthesized first in situ by adding methyllithium to a solution of dimethylthallium iodide in ether.[19] The second step is the addition of one equivalent of bis(2-pyridyl)amine (eq. 2).

$$n\,Me_2TlI \xrightarrow[]{\text{1. + n MeLi, - n LiI}\quad \text{2. + n HNPy}_2\text{ , - MeH}} [Me_2TlNPy_2]_n \qquad (2)$$

4 $n = \infty$

^{15}N-NMR-Spectroscopic Experiments

To gain information about the coordination behavior of the bis(2-pyridyl)amide ligand in the complexes **1**−**4** in solution we recorded NMR spectra. Particularly informative are the results of the ^{15}N-NMR-spectroscopic experiments. The spin of the ^{15}N nucleus is 1/2 and this gives sharp signals in the NMR experiments. Therefore, this method is particularly suitable to compare non-equivalent nitrogen atoms in solution. The chemical shift of the nucleus is correlated to its electronic shielding.

The neutral bis(2-pyridyl)amine gives rise to two signals which differ considerably with respect to their chemical shifts (assignment in analogy to similar systems[20]) because of the magnetically non-equivalent nitrogen sites (Table 1). In the aluminum and the gallium complexes **1** and **2** the signals of both nitrogen atoms display very similar chemical shifts, demonstrating the electron density to be shifted from the central nitrogen atom (the signal is more than 80 ppm downfield relative to that of the starting material) to the ring nitrogen atoms (where there is more than a 70 ppm upfield shift). These findings are further substantiated by the ^{1}H- and ^{13}C-NMR experiments. The two ^{15}N-NMR-spectroscopic shifts of both nitrogen sites in **3** and **4** differ by about 100 ppm and show a similar deviation of the signals as does the neutral system. Furthermore, in the ^{1}H- and the ^{13}C-NMR spectra of **4** the coupling of the related nuclei with the thallium nucleus are resolved ($^{2}J_{H-Tl}$ = 396.7, $^{1}J_{C-Tl}$ = 2574.7 Hz). There has no Tl−N coupling been detected. The coupling constants are in good agreement with separated linear dimethylthallium cations in solution.[21] Thus, the indium and the thallium compounds **3** and **4** are solvent-separated ion pairs in THF solution, while the aluminum and gallium complexes **1** and **2** are stable contact ion pairs, even in THF solution. To investi-

Table 1. δ ^{15}N-NMR-spectroscopic shift (THF/C_6D_6) of **1**−**4**

	Py_2NH	**1**	**2**	**3**	**4**
NC_5H_4	−107	−181	−182	−121	−117
N_{center}	−266	−184	−190	−230	−216

gate the nature of these complexes in the solid state, the crystal structures were determined.[22]

Crystal Structure of Me_2AlPy_2N (1) and Me_2GaPy_2N (2)

As in in the structures of Me_2AlPy_2CH,[8] Me_2GaPy_2CH,[8] Me_2AlPy_2P,[9] Me_2GaPy_2P[9] and Me_2AlPy_2As[9] **1** and **2** form monomers in the solid state (Figure 1). Despite the electronic competition between the deprotonated central nitrogen atom and the ring nitrogen atoms in **1** and **2** the metal center is chelated by the two ring nitrogen atoms without any contact with the central nitrogen atom (Figure 1). The anion shows *trans-trans* coordination (Scheme 4).

The Al−N distances of 191.5 pm in **1** are in good agreement with the literature values for aluminum amides,[23] but are about 15 pm shorter than the Al−N donor bonds to neutral 2,2′-bipyridyl[24a] or pyridine.[24b] The Al−C bond lengths (195.0 pm) are comparable with the distances in Me_3Al.[25] The N−Al−N angle (93.5°) is more acute than in the related bis(2-pyridyl)methyl derivative[8] (97.1°), and the aluminum atom is not in the plane of the ligand but is 28.3 pm out of the mean plane of the Py_2N^- ligand. These phenomena are due to the different "bite" of the amide ligand compared to that of the methyl ligand. The N···N distance (279.1 pm) is 7 pm shorter than in the bis(2-pyridyl)methyl ligand. In contrast to the bis(2-pyridyl)methyl ligand the amide is not strictly planar, but the pyridyl rings are twisted by 10.4° with respect to each other. The basic structural parameters of the central nitrogen atom N1 (av. N−C 134.3 pm and C−N−C 125.5°) show that this atom is sp^2-hybridized. The expected C−N−C bond angle of 120° for an unstrained system is widened by the coordinated aluminum atom. Obviously, no electron density is accumulated at the central nitrogen atom.

The gallium atom in **2**, like the aluminum atom in **1**, is coordinated to the ring nitrogen atoms (Figure 1b). It is 32.1 pm out of the plane of the anion. The two pyridyl rings are twisted by 12.1°. The slightly longer Ga−N bonds of 197.5 (N2) and 196.9 (N3) pm reflect the decrease in the covalent contribution to the metal−nitrogen bonds from aluminum to gallium, but are in good agreement with the literature values for gallium amides.[23] The Ga−C distances (Ga1−C11 194.2 and Ga1−C12 195.6 pm) are similar to the distances found for Me_3Ga in the gas phase.[26]

Crystal Structure of 3

To study the change in coordination behavior of the bis(2-pyridyl)amide anion to larger and softer cations, the bis(2-pyridyl)amine was treated with 1 equiv. of freshly prepared Me_3In.[27] The dimethylindium bis(2-pyridyl)amide (**3**) forms a dimeric structure in the solid state (Figure 2).

Figure 1. Solid-state structure of Me_2AlPy_2N (**1**) (a) and Me_2GaPy_2N (**2**) (b); anisotropic displacement parameters are depicted at a probability level of 50%

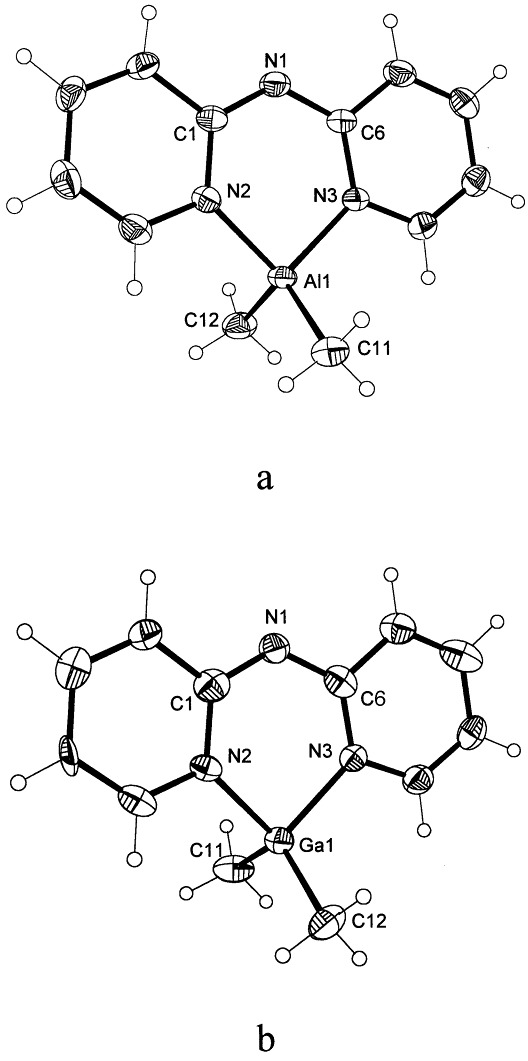
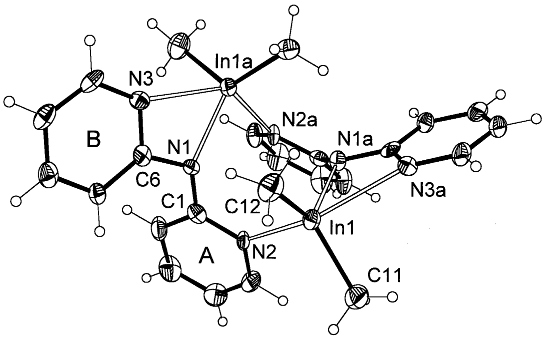


Figure 2. Solid-state structure of $[Me_2InNPy_2]_2$ (**3**); anisotropic displacement parameters are depicted at a probability level of 50%



The dimer shows C_2 symmetry with the two-fold axis in the center of the molecule. The metal atom is coordinated by the pyridyl nitrogen atoms, but they are coordinated to different metal centers, providing the links in the dimer. Additionally each indium atom is coordinated by the deprotonated central nitrogen atom. All three nitrogen atoms of the ligand are pointing in the same direction, hence, the ligand coordinates in the *cis-cis* fashion (Scheme 4). The five atoms at each metal center form a distorted trigonal-bipyramidal coordination polyhedron. C11, C12, and N1A occupy the equatorial positions (sum of the angles 355.5°) while N2 and N3A reside in the axial positions (N2−In1−N3a 138.1°). The distance of the indium atom to the central nitrogen atom (220.4 pm) is considerably shorter than that to the ring nitrogen atoms (In1−N2 236.6 and In1−N3A 261.1 pm). These distances are found in $Me_3In \cdot N$-donorbase adducts like $Me_3In \cdot$tetramethylpiperidine (250.2 pm) and have to be regarded as dative bonds[28]. Only the In1−N1 distance is in good agreement with In−N bond lengths in indium amides (av. 223.3 pm in $[Me_2InN$-methylpiperazinyl$]_2$[29]). The indium−carbon distances (213.3 and 215.1 pm) are in good agreement with the literature values of trimethylindium adducts[28] and of dimethylindium complexes[29]. In **3** the distribution of the electron density must be notably different to that in the molecules of **1** and **2**. The anionic system is less planar than in **1** and **2**. The pyridyl rings are twisted by 58.3° with respect to each other to prevent full conjugation. The bond lengths of the central nitrogen atom differ (N1−C1 138.5 and N1−C6 135.9 pm) and are longer than in **1** and **2**.

Crystal Structure of 4

In the solid-state structures of **1**−**3** the tendency to greater isolation of the dimethylmetal cation moieties Me_2M^+, (M=Al, Ga, In) in the complexes can be ascertained. These phenomena should be even more pronounced in the dimethylthallium bis(2-pyridyl)amide complex. The dimethylthallium cation is known to be a very stable fragment that often forms separated linear cations.[21] To see whether this is valid with the dipyridyl amide ligand as well, we synthesized the thallium derivative **4** from freshly synthesized trimethylthallium[19] and bis(2-pyridyl)amine. **4** crystallizes as a polymer (Figure 3).

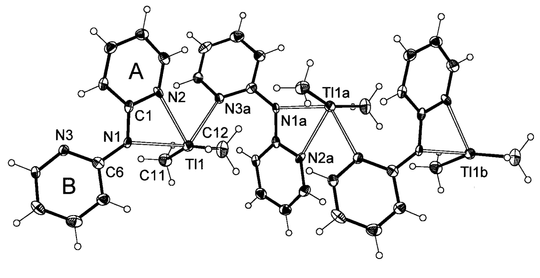


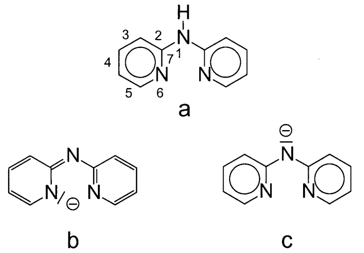
Figure 3. Solid-state structure of $[Me_2TlNPy_2]_\infty$ (**4**); anisotropic displacement parameters are depicted at a probability level of 50%

The helical polymer is made up by a crystallographic 2_1-screw axis. The thallium atoms are coordinated by the two methyl carbon atoms and three nitrogen atoms of the anionic ligand, but it seems arbitrary to assign any coordination polyhedron to the metal atom. It seems worth noting that in **4** the *cis-trans* arrangement (Scheme 4) of the bis(2-pyridyl)amide ligand is observed for the first time. The central, as well as one ring nitrogen atom (N1 and N2 in Figure 3), coordinate to the same metal center (Tl1), while the second ring (B in Figure 3) turns about the central N−C bond and coordinates to a second metal center (Tl1a) providing the polymeric link. The pyridyl rings are twisted by 38.2° with respect to each other to prevent full conjugation of the Py_2N^- anion. In contrast to **3** the shortest M−N distance is not found to be to the central nitrogen but to one ring nitrogen atom (Tl1−N2 248.1 pm). The other two are considerably longer (Tl1−N1 259.2; Tl2−N3a 268.9 pm). However, all three Tl−N contacts have to be regarded as weak donor bonds, since Tl−N bonds in thallium amides are normally shorter.[30] The Tl−C bonds are similar in length to those determined for the Me_2M^+ cations[21], but about 8 pm shorter than the shortest Tl−C contact in Me_3Tl.[31] The Me_2M^+ cation is almost linear (C11−Tl1−C12 158.3°), only bent slightly by the additional weak coordination of the three nitrogen atoms to the open side.

Structural Comparison

As mentioned above, the MMe_2 fragment in the complexes approaches linearity as the Group-13 metal gets heavier. The C−M−C angle widens from 116.9 (M = Al) to 120.8 (M = Ga), 126.1 (M = In) and finally to 158.3° (M = Tl). Hence the Me_2M^+ cationic character is most pronounced in the In and Tl complexes. The contacts to the Py_2N^- anion in the aggregates of **3** and **4** are only weak, while the hard metals, aluminum in **1** and gallium in **2**, induce metal amide bond lengths on the molecular level.

Table 2. Bond lengths [pm] of the Py_2N^- anion in **1**−**4** compared to the starting material



Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Py_2NH (a)	138.0	139.5	137.0	137.0	136.5	134.0	133.5
1 and **2**	134.5	141.7	136.0	139.4	135.6	136.3	136.4
3 A[a]	138.5	140.6	137.3	137.5	135.8	135.9	134.0
3 B[a]	135.9	140.4	137.2	137.9	136.9	134.1	136.1
4 A[a]	136.2	143.0	137.5	139.2	137.1	132.3	135.1
4 B[a]	134.8	140.6	133.7	140.3	135.8	134.5	137.1

[a] A and B refer to the ring labeling in Figures 2 and 3.

The bis(2-pyridyl)amide ligand itself reveals different coordination behavior toward small hard and large soft cations in solution and in the solid state. In the compounds with the hard aluminum and gallium cations the anion exclusively coordinates the metal centers through the two ring nitrogen atoms. This coordination mode has previously been observed in aluminum and gallium complexes of the bis(2-pyridyl)methyl anion.[8] Coordination of the ring nitrogen atoms and the ^{15}N-NMR-specroscopic shift lead the negative charge in **1** and **2** to be accumulated at the ring hetero atoms. In **3** and **4** the NMR experiments in solution, and the coordination through the central nitrogen atom in the solid state, indicate an accumulation of negative charge at this position. This different electronic situation has to induce structural differences in the Py_2N^- anion. Close inspection of the solid-state structures should be decisive in determining whether the resonance form **b**, with the charge at the ring nitrogen atom and localized double bonds in the rings, or the mesomeric form **c**, with the charge at the central nitrogen atom and delocalized rings, contributes most to the description of the structures (Table 2).

All experiments prove that **b** is the form which contributes most for **1** and **2**. Unlike the neutral system[32] described in **a** the double bonds are localized in positions 1, 3, and 5. The bonds 6 and 7 of the pyridyl nitrogen atom are lengthened significantly, also indicating as well an accumulation of the negative charge on these nitrogen atoms. In **3** and **4** the bonding situation is more complex. The pyridyl rings are not coplanar and both are involved in a different coordination. The notation A and B refers to the two different rings in Figures 2 and 3, respectively. Ring A in **3** is similar to the delocalized rings of bis(2-pyridyl)amide. Ring B, however, exhibits significant deviations from the neutral molecule. The bond in position 1 is shortened by 2.1 pm, and that in position 7 is lengthened by 2.6 pm, relative to the amine. Coupling of the central nitrogen atom to ring B and the marginal shift of electron density from the original place of deprotonation to the pyridyl ring B are established in this structure. Both nitrogen atoms are members of the azaallyl system coordinated to the same indium atom to give an InN_2C four-membered ring. In **4** significant shift of electron density to ring B can be detected. The bond in position 1 is shortened by 3.2 pm and there is partial localization of double bonds in the positions 3 and 5. As a consequence the $Tl-N_{ring}$ bond is more than 11 pm shorter than the $Tl-N_{central}$ bond. The nitrogen atom of the delocalized ring A provides the longest metal donor bond (about 21 pm longer).

Conclusion

The bis(2-pyridyl)methyl and the bis(2-pyridyl)phosphide anions coordinate metal atoms exclusively through the nitrogen atoms within the pyridyl rings. Due to the electropositive bridgehead atoms these ligands behave like amides with the electron density accumulated at the ring nitrogen atoms. The bis(2-pyridyl)amides discussed here show a higher coordination flexibility towards metals. The electronic equivalence of the central and the ring nitrogen atoms leaves the energetic hyperface of the anion quite flat and the electron density is polarized according to the requirements of the metal. In the complexes with the hard metal aluminum (**1**) and gallium (**2**) the coordination is the same as that observed in the bis(2-pyridyl)methyl and -phosphide ligands. With the soft metals indium and thallium the system changes its coordination behavior to suit the larger, and easier to polarize, cations. In these complexes the deprotonated nitrogen atom participates in the coordination and the ligand forms a bridging group. In the indium complex **3** the *cis-cis* orientation gives rise to a dimeric structure, while the unprecedented *cis-trans* arrangement in the thallium compound **4** leads to a polymeric structure in the solid state. In the aluminum and the gallium complexes **1** and **2** the metal−nitrogen bond lengths are in good agreement with literature values for metal amides. In the indium and thallium complexes most metal−nitrogen distances are too long for metal amides, partly due to their higher aggregation. They approach separated Me_2M^+ and Py_2N^- residues, even in the solid state. In solution the Al and Ga complexes are close contact ion pairs while the In and Tl complexes dissolve as solvent-separated ion pairs. Hence, not only the steric requirements of N-heteroaromatic ligands have to be considered in molecular self-assembling processes, but also the inductive effect of different metal fragments (like in any complexation).

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Experimental Section

All manipulations were performed under dry nitrogen with Schlenk techniques or in an argon drybox. Solvents were dried over Na/K alloy and distilled prior to use. NMR spectra were obtained with a Bruker MSL 400 or AM 250 instrument. All NMR spectra were recorded in C_6D_6 or $[D_8]$THF with $SiMe_4$ (^{1}H, ^{13}C), CH_3NO_2 (^{15}N) and $AlCl_3$ (^{27}Al) as external standards. EI mass spectra were measured with Finnigan MAT 8230 or Varian MAT CH 5 instruments.

1: 1.00 g (5.8 mmol) of $HN(2\text{-}NC_5H_4)_2$ in 25 ml of Et_2O was treated with an equimolar amount of Me_3Al (2.90 ml of a 2.0 M solution) at −10°C. Stirring for 12 h at room temp. gave a yellow solution with a little of a yellow precipitate. Addition of 5 ml of THF gave a clear solution. Crystallization from this solution at −35°C yielded crystals suitable for X-ray diffraction. Yield 0.78 g (80%), m.p. 146°C. − ^{1}H NMR ($[D_8]$THF, room temp.): $\delta = -0.66$ (s, CH_3), 6.68 (ddd, $^3J_{5,4}$ 6.8 Hz, $^3J_{5,6} = 6.1$ Hz, $^4J_{5,3} = 1.2$ Hz, 5-H), 6.93 (ddd, $^3J_{3,4} = 8.8$ Hz, $^4J_{3,5} = 1.2$ Hz, $^5J_{3,6} = 0.9$ Hz, 3-H), 7.54 (ddd, $^3J_{4,3} = 8.8$ Hz, $^3J_{4,5} = 6.8$ Hz, $^4J_{4,6} = 1.9$ Hz, 4-H), 7.74 (ddd, $^3J_{6,5} = 6.1$ Hz, $^4J_{6,4} = 1.9$ Hz, $^5J_{6,3} = 0.9$ Hz, 6-H). − ^{13}C NMR (THF/C_6D_6, room temp.): $\delta = -10.5$ (s, CH_3), 112.9 (s, C-5), 124.8 (s, C-3), 139.2 (s, C-4), 140.5 (s, C-6), 158.6 (s, C-2). − ^{15}N NMR (THF/C_6D_6, room temp.): $\delta = -181.1$ (s, NC_5H_4), −184.5 (s, N_{center}). − ^{27}Al NMR (THF/C_6D_6, room temp.): $\delta = 150$. − MS (70 eV); *m/z* (%): 227 (14) $[Me_2Al(NC_5H_4)_2N]$, 212 (100) $[MeAl(NC_5H_4)_2N]$, 197 (10) $[Al(NC_5H_4)_2N]$, 120 (10) $[Al(NC_5H_4)N]$, 106 (14) $[Al(NC_5H_4)]$.

2: 4.00 g (34.8 mmol) of Me_3Ga in 50 ml toluene was treated with 5.96 g (34.8 mmol) of $HN(2\text{-}NC_5H_4)_2$, dissolved in 20 ml of toluene, at −78°C. Stirring for 12 h at room temp. gave a yellow solution. Crystallization from this solution at −35°C for 3 d yielded crystals in the form of pale yellow needles suitable for X-ray diffraction. Yield 7.48 g (80%), m.p. 134°C. − ^{1}H NMR ($[D_8]$THF, room temp.): $\delta = -0.10$ (s, CH_3), 5.97 (ddd, $^3J_{4,5} = 6.8$ Hz, $^3J_{4,3} = 6.0$ Hz, $^4J_{4,6} = 1.3$ Hz, 4-H), 6.83 (ddd, $^3J_{5,6} = 8.8$ Hz,

$^3J_{5,4}$ = 6.8 Hz, $^4J_{5,3}$ = 2.0 Hz, 5-H), 7.05 (ddd, $^3J_{3,4}$ = 6.0 Hz, $^4J_{3,5}$ = 2.0 Hz, $^5J_{3,6}$ = 0.8 Hz, 3-H), 7.09 (ddd, $^3J_{6,5}$ = 8.8 Hz, $^4J_{6,4}$ = 1.3 Hz, $^5J_{6,3}$ = 0.8 Hz, 6-H). − ^{13}C NMR (THF/C_6D_6, room temp.): δ = −7.5 (s, CH_3), 112.4 (s, C-5), 124.7 (s, C-3), 138.2 (s, C-4), 141.1 (s, C-6), 158.6 (s, C-2). − ^{15}N NMR (THF/C_6D_6, room temp.): δ = −181.5 (s, *N*C_5H_4), −189.8 (s, N_{center}). − MS (70 eV); *m*/*z* (%): 269 (14) [$Me_2Ga(NC_5H_4)_2N$], 254 (100) [$MeGa(NC_5H_4)_2N$], 238 (24) [$Ga(NC_5H_4)_2N$].

3: 1.80 g (11.3 mmol) of Me_3In in 10 ml of toluene was treated with 1.93 g (11.3 mmol) of $HN(2\text{-}NC_5H_4)_2$, dissolved in 10 ml of toluene at room temp. Stirring for 24 h at room temp. gave a colorless precipitate. Heating under reflux for 1 h gave a clear solution. Colorless needles crystallized upon cooling the solution slowly to room temp. These crystals were suitable for X-ray diffraction. Yield 3.10 g (89%), m.p. 208°C. − ^{1}H NMR (C_6D_6, room temp.): δ = 0.24 (s, CH_3), 6.11 (dd, $^3J_{5,4}$ = 7.2 Hz, $^3J_{5,6}$ = 5.0 Hz, 5-H), 6.68 (d, $^3J_{3,4}$ = 8.2 Hz, 3-H), 6.92 (dd, $^3J_{4,3}$ = 8.2 Hz, $^3J_{4,5}$ = 7.2 Hz, 4-H), 7.77 (d, $^3J_{6,5}$ = 5.0 Hz, 6-H). − ^{13}C NMR (C_6D_6, room temp.): δ = −5.3 (s, CH_3), 113.5 (s, C-5), 114.0 (s, C-3), 138.7 (s, C-4), 147.1 (s, C-6), 163.2 (s, C-2). − ^{15}N NMR (THF/C_6D_6, room temp.): δ = −120.7 (s, *N*C_5H_4), −230.2 (s, N_{center}). − MS (70 eV); *m*/*z* (%): 315 (20) [$Me_2InN(NC_5H_4)_2$], 300 (100) [$MeInN(NC_5H_4)_2$], 285 (68) [$InN(NC_5H_4)_2$], 170 (78) [$N(NC_5H_4)_2$], 145 (24) [Me_2In].

4: 2.00 g (5.5 mmol) of Me_2TlI in 30 ml of *n*-hexane was treated with 3.44 ml (5.5 mmol) of a 1.6 M solution of MeLi in Et_2O at room temp. After stirring for 2 h, a solution of 0.95 g (5.5 mmol) of $HN(2\text{-}NC_5H_4)_2$ in 20 ml of Et_2O was added. This reaction mixture was stirred for 24 h at room temp. The solvent was removed under vacuum and the precipitate was suspended in toluene and the LiI was removed by filtration. Colorless needles crystallized from the clear solution at room temp. These crystals were suitable for X-ray diffraction. Yield 1.12 g (50%), m.p. 179°C. − ^{1}H NMR (C_6D_6, room temp.): δ = 0.82 (d, $^2J_{Me-Tl}$ = 396.7 Hz, CH_3), 6.35 (ddd, $^3J_{5,4}$ = 7.0 Hz, $^3J_{5,6}$ = 5.1 Hz, $^4J_{5,3}$ = 1.0 Hz, 5-H), 7.10 (ddd, $^3J_{3,4}$ = 8.5 Hz, $^4J_{3,5}$ = 1.1 Hz, $^5J_{3,6}$ = 0.9 Hz, 3-H), 7.22 (ddd, $^3J_{4,3}$ = 8.5 Hz, $^3J_{4,5}$ = 7.0 Hz, $^4J_{4,6}$ = 2.0 Hz, 4-H), 8.06 (ddd, $^3J_{6,5}$ = 5.1 Hz, $^4J_{6,4}$ = 2.0 Hz, $^5J_{6,3}$ = 0.9 Hz, 6-H). − ^{13}C NMR (THF/C_6D_6, room temp.): δ = 8.7 (d, $^1J_{Me-Tl}$ = 2574.7 Hz, CH_3), 112.1 (s, C-5), 112.9 (s, C-3), 137.4 (s, C-4), 147.3 (s, C-6), 161.1 (s, C-2). − ^{15}N NMR (THF/C_6D_6, room temp.): δ = −117.3 (s, *N*C_5H_4), −215.8 (s, N_{center}). − MS (70 eV); *m*/*z* (%): 405 (26) [$Me_2TlN(NC_5H_4)_2$], 390 (36) [$MeTlN(NC_5H_4)_2$], 375 (90) [$TlN(NC_5H_4)_2$], 235 (18) [Me_2Tl], 205 (100) [Tl], 170 (20) [$N(NC_5H_4)_2$].

X-ray Measurements of **1−4**: All data were collected at low temperatures using an oil-coated shock-cooled crystal[33] on a Stoe-

Table 3. Selected bond lengths [pm] and angles [°] of **1−4**

1		**2**		**3**		**4**	
N1−C1	134.3(2)	N1−C1	133.9(13)	N1−C1	138.5(7)	N1−C1	136.2(9)
N1−C6	134.2(2)	N1−C6	135.4(12)	N1−C6	135.9(7)	N1−C6	134.8(10)
				In1−N1A	220.4(5)	Tl1−N1	259.2(7)
Al1−N2	191.6(2)	Ga1−N2	197.5(7)	In1−N2	236.6(5)	Tl1−N2	248.1(7)
Al1−N3	191.4(2)	Ga1−N3	196.9(7)	In1 N3A	261.1(5)	Tl1 N3A	268.9(6)
Al1−C(av)	195.0	Ga1−C(av)	194.9	In1−C (av)	214.2	Tl1−C (av)	213.4
C1−N1−C6	125.5(2)	C1−N1−C6	127.6(8)	C1−N1−C6	121.1(5)	C1−N1−C6	124.5(7)
C11−Al1−C12	116.9(1)	C11−Ga1−C12	120.8(4)	C11−In1−C12	126.1(3)	C11−Tl1−C12	158.3(4)

Table 4. Crystal data for **1−4** at 153 K

	1	**2**	**3**	**4**
Formula	$C_{12}H_{14}AlN_3$	$C_{12}H_{14}GaN_3$	$C_{12}H_{14}InN_3$	$C_{12}H_{14}TlN_3$
Mol. mass	227.2	270.0	315.1	404.6
Cryst. size [mm]	0.5 × 0.3 × 0.3	0.3 × 0.2 × 0.2	0.4 × 0.2 × 0.2	0.2 × 0.2 × 0.2
Space group	*Pbca*	*Pbca*	$P2_12_12$	$P2_12_12_1$
a [pm]	692.5(1)	692.5(1)	1633.7(3)	710.5(1)
b [pm]	1233.4(2)	1238.5(2)	789.3(2)	1099.7(2)
c [pm]	2779.9(4)	2775.0(6)	974.9(2)	1555.6(3)
V [nm^3]	2.374(1)	2.380(1)	1.257(1)	1.215(1)
Z	8	8	4	4
T [K]	153(2)	153(2)	153(2)	153(2)
ρ_c [Mgm^{-3}]	1.271	1.507	1.665	2.211
μ [mm^{-1}]	0.146	2.288	1.857	13.264
F(000)	960	1104	624	752
2Θ range [°]	8−50	8−45	8−45	8−55
No. of refln measd.	3749	3505	3045	1630
No. of unique reflns.	2103	1548	1654	1625
No. of restraints	28	0	0	0
Refined param.	181	147	147	147
*R*1[a] [$I > 2\sigma(I)$]	0.040	0.061	0.028	0.029
*wR*2[b] (all data)	0.115	0.183	0.066	0.071
*g*1; *g*2[c]	0.072; 0.423	0.075; 17.187	0.031; 0.010	0.045; 0.436
Flack *x* param.			−0.008(61)	0.003(22)
Highest diff peak (10^{-6} e pm^{-3})	0.25	0.89	0.76	0.72
Absorbt. corr.		semi-empirical	semi-empirical	semi-empirical
Trans. min; max		0.499; 0.993	0.562; 0.870	0.617; 1.000

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. − [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. − [c] $w = 1/[\sigma^2(F_o^2) + (g1\cdot P)^2 + g2\cdot P]$; $P = (F_o^2 + 2F_c^2)/3$.

Siemens AED diffractometer with Mo-K_α (λ = 71.073 pm) radiation. A semiempirical absorption correction[34] was employed for structures **2**−**4**. The structures were solved by direct methods using SHELXS-90[35] and refined with all data on F^2 with a weighting scheme using SHELXL-93.[36] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the molecules were geometrically idealized and refined using a riding model. Refinement of an inversion twin parameter[37] [$x = -0.008(61)$ (**3**), 0.003(22) (**4**) where $x = 0$ for the correct absolute structure and +1 for the inverted structure] confirmed the absolute structures of **3** and **4**. Selected bond lengths and angles of **1**−**4** can be found in Table 3, relevant crystallographic data for **1**−**4** are presented in Table 4. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100792. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) + 44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk].

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[1] [1a] A. R. Katritzky, J. M. Lagowski, *The Principles of Heterocyclic Chemistry*, Methuen, London, **1967**. – [1b] J. A. Joule, G. F. Smith, *Heterocyclic Chemistry*, Van Nostrand Reinhold, London, **1978**. – [1c] G. R. Newkome, W. W. Paudler, *Contemporary Heterocyclic Chemistry*, Wiley, New York, **1982**. – [1d] A. R. Katritzky, C. W. Rees, *Comprehensive Heterocyclic Chemistry*, Pergamon, Oxford, **1984**. – [1e] J. Reedijk, in *Comprehensive Coordination Chemistry* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), vol. 2, Pergamon, Oxford, **1987**, p. 73. – [1f] T. Eicher, S. Hauptmann, *Chemie der Heterocyclen*, Georg Thieme Verlag, Stuttgart, New York, **1994**. – [1g] A. Togni, L. M. Venanzi, *Angew. Chem.* **1994**, *106*, 517; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 497. – [1h] D. T. Davies, *Aromatische Heterocyclen*, VCH, Weinheim, **1995**.

[2] [2a] F. Blau, *Ber. Dtsch. Chem. Ges.* **1888**, *84*, 85. – [2b] E. C. Constable, P. J. Steel, *Coord. Chem. Rev.* **1989**, *93*, 205. – [2c] P. J. Steel, *Coord. Chem. Rev.* **1990**, *106*, 227. – [2d] C. E. Kriley, P. E. Faucrick, I. P. Rothwell, *J. Am. Chem. Soc.* **1994**, *116*, 5225.

[3] [3a] J.-M. Lehn, *Science* **1985**, *227*, 849. – [3b] J.-M. Lehn, *Angew. Chem.* **1990**, *102*, 1347; *Angew. Chem. Int. Ed. Eng.* **1990**, *29*, 1304. – [3c] E. C. Constable, *Angew. Chem.* **1991**, *103*, 1482; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1450. – [3d] J.-M. Lehn, *J. Coord. Chem.* **1992**, *27*, 3. – [3e] E. C. Constable, M. J. Hannon, D. A. Tocher, *Angew. Chem.* **1992**, *104*, 218, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 230. – [3f] E. C. Constable, A. J. Edwards, P. R. Raithby, J. V. Walker, *Angew. Chem.* **1993**, *105*, 1486; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1465. – [3g] A. Williams, *Chem. Eur. J.* **1997**, *3*, 15. – [3h] H. Plenio, *Angew. Chem.* **1997**, *109*, 358; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 348.

[4] M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi, K. Ogura, *Nature* **1995**, *378*, 469.

[5] [5a] H.-J. Schneider, H. Dürr, *Frontiers in Supramolecular Organic Chemistry and Photochemistry*, VCH, Weinheim, **1991**, 12. – [5b] A. Harriman, R. Ziessel, *J. Chem. Soc., Chem. Commun.* **1996**, 1707.

[6] For recent review: T. Kottke, D. Stalke, *Chem. Ber.* **1997**, 130, 1365.

[7] U. Pieper, D. Stalke, *Organometallics* **1993**, *12*, 1201.

[8] [8a] H. Gornitzka, D. Stalke, *Angew. Chem.* **1994**, *106*, 695; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 693. – [8b] H. Gornitzka, D. Stalke, *Organometallics* **1994**, *13*, 4398.

[9] [9a] A. Steiner, D. Stalke, *J. Chem. Soc., Chem. Commun.* **1993**, 444. – [9b] A. Steiner, D. Stalke, *Organometallics* **1995**, *14*, 2422.

[10] [10a] A. Steiner, D. Stalke, *J. Chem. Soc., Chem. Commun.* **1993**, 1702. – [10b] A. Steiner, D. Stalke, *Inorg. Chem.* **1995**, *34*, 4846.

[11] D. S. Lawrence, T. Jiang, M. Levett, *Chem. Rev.* **1995**, *95*, 2229.

[12] G. S. Hanan, J.−M. Lehn, N. Kyritsakas, J. Fischer, *J. Chem. Soc., Chem. Commun.* **1995**, 765.

[13] [13a] N. Ray, S. Tyagi, B. Hathaway , *J. Chem. Soc., Dalton Trans.* **1982**, 143. – [13b] E. Spodine, A. M. Atria, R. Baggio, M. T. Garland, *Acta Crystallogr., Sect. C* **1996**, *52*, 1407. – [13c] E. A. Griffith, H.−Y. Li, E. L. Amma, *Inorg. Chim. Acta* **1988**, *148*, 203. – [13d] R. A. Howie, G. Izquierdo, G. P. McQuillian, *Inorg. Chim. Acta* **1983**, *72*, 165.

[14] [14a] O. R. Rodig, T. Brückner, B. K. Hurlburt, R. K. Schlatzer, T. L. Venable, E. Sinn, *J. Chem. Soc., Dalton Trans.* **1981**, 196. – [14b] J. F. Geldard, F. Lions, *J. Am. Chem. Soc.* **1962**, *84*, 2262. – [14c] H. C. Freeman, M. R. Snow, *Acta Crystallogr., Sect. C* **1965**, *18*, 843.

[15] B. S. Creavav, G. V. Gallagher, R. A. Howle, C. Long, G. P. Mcquillian, unpublished results, quoted as ref. [17] in ref.[14c].

[16] G. B. Deacon, S. J. Faulks, B. M. Gatehouse, A. Jozsa, *J. Inorg. Chim. Acta* **1977**, *21*, L1.

[17] P. Akhter, J. Hathaway, unpublished results, quoted as ref. [22] in ref.[14c].

[18] [18a] L.-P. Wu, P. Field, T. Morrissey, C. Murphy, P. Nagle, B. Hathaway, C. Simmons, P. Thornton, *J. Chem. Soc., Dalton Trans.* **1990**, 3835. – [18b] S. Aduldecha, B. Hathaway, *J. Chem. Soc., Dalton Trans.* **1991**, 993.

[19] H. Gilman, R. G. Jones, *J. Am. Chem. Soc.* **1946**, *68*, 517.

[20] [20a] C. Gatti, A. Ponti, A. Gamba, G. Pagani, *J. Am. Chem. Soc.* **1992**, *114*, 8634. – [20b] G. C. Levi, R. L. Lichter, *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*, Wiley, New York, **1979**. – [20c] G. J. Martin, L. M. Maryvonne, J.-P. Gonesnard, *^{15}N-NMR Spectroscopy*, Springer, Berlin, **1981**.

[21] [21a] G. D. Shier, R. S. Drago, *J. Organomet. Chem.* **1966**, *5*, 330. – [21b] A. G. Lee, "The Chemistry of Thallium" in *Topics in Inorganic and General Chemistry* (Ed.: P. L. Robinson), Elsevier, Amsterdam, **1971**.

[22] The structure-determining factors of the cations towards "carbanions" have been investigated by i. e.: C. Lambert, P. v. R. Schleyer, *Angew. Chem.* **1994**, *106*, 1187; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1129.

[23] [23a] K. M. Waggoner, P. P. Power, *J. Am. Chem. Soc.* **1991**, *113*, 3385. – [23b] M. Veith, A. Spaniol, J. Pöhlmann, F. Gross, V. Huch, *Chem. Ber.* **1993**, *126*, 2625.

[24] [24a] P. L. Bellavance, E. R. Corey, J. Y. Corey, G. W. Hey, *Inorg. Chem.* **1977**, *16*, 462. – [24b] P. Pullmann, K. Hensen, J.W. Bats, *Z. Naturforsch., B* **1982**, *37*, 1312.

[25] [25a] R. G. Vranka, E. L. Amma, *J. Am. Chem. Soc.* **1967**, *89*, 3121. – [25b] S. K. Byram, J. K. Fawcett, S. C. Nyburg, R. J. O'Brien, *J. Chem. Soc., Chem. Commun.* **1970**, 16. – [25c] J. C. Huffmann, W. E. Streib, *J. Chem. Soc., Chem. Commun.* **1971**, 911.

[26] B. Beagley, D. G. Schmidling, I. A. Steer, *J. Mol. Struct.* **1974**, *21*, 437.

[27] H. C. Clark, A. L. Pickard, *J. Organomet. Chem.* **1967**, *8*, 427.

[28] D. C. Bradley, H. Dawes, D. M. Frigo, M. B. Hursthouse, B. Hussain, *J. Organomet. Chem.* **1987**, *325*, 55.

[29] [29a] A. M. Arif, D. C. Bradley, H. Dawes, D. M. Frigo, M. B. Hursthouse, B. Hussain, *J. Chem. Soc., Dalton Trans.* **1987**, 2159. – [29b] M. A. Petrie, K. Ruhlandt-Senge, H. Hope, P. P. Power, *Bull. Soc. Chim. Fr.* **1993**, *130*, 851.

[30] [30a] K. W. Hellmann, L. H. Gade, A. Steiner, D. Stalke, F. Möller, *Angew. Chem.* **1997**, *109*, 99; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 160. – [30b] K. W. Hellmann, L. H. Gade, R. Fleischer, D. Stalke, *J. Chem. Soc., Chem. Commun.* **1997**, 527. – [30c] K. W. Hellmann, L. H. Gade, R. Fleischer, T. Kottke, *Chem. Eur. J.* **1997**, *3*, 1801.

[31] G. M. Sheldrick, W. S. Sheldrick, *J. Chem. Soc.* **1970**, 128.

[32] [32a] J. E. Johnson, R. A. Jacobson, *Acta. Crystallogr., Sect. B* **1973**, *29*, 1669. – [32b] G. I. Pyrka, A. A. Pinkerton, *Acta. Crystallogr., Sect.C* **1992**, *48*, 91.

[33] [33a] T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615. – [33b] T. Kottke; R. J. Lagow, D. Stalke, *J. Appl. Crystallogr.* **1996**, *29*, 465.

[34] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr., Sect. A* **1968**, *24*, 351.

[35] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[36] G. M. Sheldrick, *SHELXL-93, Program for Crystal Structure Refinement*, University of Göttingen, **1993**.

[37] [37a] H. D. Flack, *Acta Crystallogr., Sect. A* **1983**, 39, 876. – [37b] G. Bernardinelli, H. D. Flack, *Acta Crystallogr., Sect. A* **1985**, *41*, 500.

[97243]