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Coordination of the Bis(pyridyl)methyl Substituent to Group 1 and 13 Metals

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The bis(pyridyl)methyl derivatives $[(thf)_2Li(2\text{-}NC_5H_4)_2CH]$, $[H_2C(2\text{-}NC_5H_4)_2Li(2\text{-}NC_5H_4)_2CH]$, $[Li(12\text{-}crown\text{-}4)_2][Li\{(2\text{-}NC_5H_4)_2CH\}_2]$, $[Na(thf)_6][Li\{(2\text{-}NC_5H_4)_2CH\}_2]$, $[Me_2Al(2\text{-}NC_5H_4)_2CH]$, and $[Me_2Ga(2\text{-}NC_5H_4)_2CH]$ have been synthesized and characterized by low-temperature X-ray structure determination. Although deprotonated at the central carbon atoms, they are only formally carbanions. All experimental structural parameters indicate that they are better described as amides. The bis(pyridyl)methyl ligand coordinates lithium, aluminum, and gallium with both nitrogen ring atoms. All anions are planar and fully conjugated. Two anions coordinated to a single lithium atom seem favorable, because this structural motif of the overall anion is present in the structure of a lithium lithiate and a sodium lithiate. In the first structure, the lithium cation is complexed by two crown ether molecules, in the latter, the sodium cation is complexed by six thf molecules. Crystals of this compound melt at about −30 °C. At −80 °C, it is possible to isolate an intermediate with lithium coordinated by one bis(pyridyl)methyl anion and one molecule bis(pyridyl)methane, which donates the lithium atom like a nitrogen base. This intermediate gives direct access to the structural comparison of the starting material and the anion. In all metal complexes, the double bonds of the anion are localized, regardless of group 1 or group 13 metals. Lithium, aluminum, and gallium match in size and fit the bite of the bis(pyridyl)methyl ligands. The bigger sodium cation is complexed by thf molecules.

Introduction

Recently, we have been interested in comparing the coordinative behavior of the triphenylmethyl carbanion[1] to that of the diphenylpyridylmethyl substituent[2] toward alkali metals. While the Ph_3C^- anion is capable of delocalizing the negative charge to a maximum extent, leaving the potential energy surface quite flat,[3−5] $Ph_2(2\text{-}NC_5H_4)C^-$ seems to have a distinct minimum. The harder cations Li^+ and Na^+ are located above the central carbon atom[6−9] in Ph_3C^-, but the bigger cations like K^+, Rb^+, and Cs^+ are located above the center of one phenyl ring.[1] The $Ph_2(2\text{-}NC_5H_4)C^-$-anion seems only formally to be a carbanion. The negative charge, however, is almost entirely located at the nitrogen atom. Not only Li^+ and Na^+ but also K^+ are coordinated to the nitrogen atom of the $Ph_2(2\text{-}NC_5H_4)C$ amide.[2] With this in mind, we have turned our attention to the $(2\text{-}NC_5H_4)_2CH^-$ anion.[10]

$[(thf)_2Li(2\text{-}NC_5H_4)_2CH]$ (**1**), $[H_2C(2\text{-}NC_5H_4)_2Li(2\text{-}NC_5H_4)_2CH]$ (**2**), $[Li(12\text{-}crown\text{-}4)_2][Li\{(2\text{-}NC_5H_4)_2CH\}_2]$ (**3**), and $[Na(thf)_6][Li\{(2\text{-}NC_5H_4)_2CH\}_2]$ (**4**) have been synthesized and characterized by low-temperature X-ray structures. To study the coordination of the $(2\text{-}NC_5H_4)_2CH$ ligand toward group 13 metals, we have synthesized $[Me_2Al(2\text{-}NC_5H_4)_2CH]$ (**5**) and $[Me_2Ga(2\text{-}NC_5H_4)_2CH]$ (**6**). Their structures are presented as well.

Results and Discussion

Preparation of 1−6. Bis(2-pyridyl)methane was prepared according to the literature.[11−13] Compound **1** was synthesized by adding *n*-butyllithium to a bis(2-pyridyl)methane solution (eq 1).

$$(2\text{-}NC_5H_4)_2CH_2 + {}^nBuLi \xrightarrow{-80\ °C\ \text{in THF}} \underset{\mathbf{1}}{[(thf)_2Li(2\text{-}NC_5H_4)_2CH]} + {}^nBuH \quad (1)$$

If bis(2-pyridyl)methane is reacted with *n*-butyllithium in hydrocarbons like toluene, the intermediate **2** can be isolated at −80 °C. In **2**, 1 equiv of the starting material acts as a donor base (well-known in lithium chemistry; like tmeda $Me_2NCH_2CH_2NMe_2$), while the second forms the deprotonated anion (eq 2). **2** decomposes at temperatures slightly higher than −50 °C. The colorless crystals turn into a dark brown oil. **1** was reacted with 1 equiv of 12-crown-4. The lithium lithiate **3** was isolated (eq 3). To achieve metal exchange, **1** was

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$$2(2\text{-}NC_5H_4)CH_2 + 2\,{}^nBuLi \xrightarrow{-80\ ^\circ C\ \text{in toluene}} \underset{\mathbf{2}}{[H_2C(2\text{-}NC_5H_4)_2Li(2\text{-}NC_5H_4)_2CH]} + {}^nBuLi + {}^nBuH \quad (2)$$

$$2\underset{\mathbf{1}}{[(thf)_2Li(2\text{-}NC_5H_4)_2CH]} + 2\,(12\text{-crown-4}) \xrightarrow{-80\ ^\circ C\ \text{in hexane/THF}} \underset{\mathbf{3}}{[Li(12\text{-crown-4})_2][Li\{(2\text{-}NC_5H_4)_2CH\}_2]} \quad (3)$$

reacted in a 1:1 ratio with NaO^{t}Bu. Only 0.5 equiv of Li$^+$ in **1** was substituted by Na$^+$, resulting in the sodium lithiate **4** (eq 4). The colorless crystals of **4** melt at ca. −30 °C. **1** was reacted with dimethylaluminum chloride and dimethylgallium chloride to give the dimethylaluminum bis(pyridyl)methyl (**5**) and dimethylgallium bis(pyridyl)methyl (**6**) derivatives (eq 5).

$$2\underset{\mathbf{1}}{[(thf)_2Li(2\text{-}NC_5H_4)_2CH]} + 2NaO^tBu \xrightarrow{\text{room temp in THF}} \underset{\mathbf{4}}{[Na(thf)_6][Li\{(2\text{-}NC_5H_4)_2CH\}_2]} + NaO^tBu + LiO^tBu \quad (4)$$

$$\underset{\mathbf{1}}{[(thf)_2Li(2\text{-}NC_5H_4)_2CH]} + Me_2MCl \xrightarrow{-80\ ^\circ C} [Me_2M(2\text{-}NC_5H_4)_2CH] + LiCl \quad (5)$$

5: M = Al; in Et$_2$O
6: M = Ga; in toluene

5 and **6** can be synthesized using a second route. Reacting bis(2-(pyridyl)methane directly with Me$_3$Al or Me$_3$Ga yields the product and methane.

Crystal Structure of 1. As in the structures of Ph$_2$(2-NC$_5$H$_4$)CLi·2Et$_2$O[2], the lithium atom in **1** is not coordinated to the central deprotonated carbon atom (Figure 1; Table 1), but it is bound to both nitrogen atoms of the pyridyl rings. The Li−N distances of 196.6 and 197.3 pm are similar to those in lithium amides,[14] which might be taken as the first hint that the derivatives discussed here are amides rather than carbanion-containing compounds.

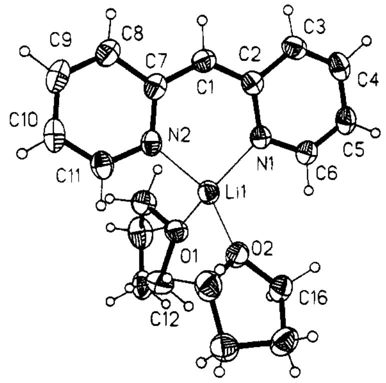

Figure 1. Crystal structure of **1**, anisotropic displacement parameters depicting 50% probability.

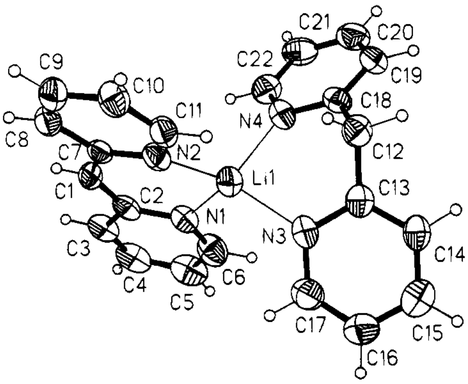

Figure 2. Crystal structure of **2**, anisotropic displacement parameters depicting 50% probability. The uncoordinated lattice toluene molecule has been omitted for clarity.

The chelating anion is essentially planar. The mean deviation from the plane of the eleven carbon and two nitrogen atoms of the anion is only 4 pm. The lithium atom also lies in that plane (deviation 3.6 pm). The basic structural parameters of the central carbon atom C1 (C1−C2 and C1−C7, 140.6 pm; C2−C1−C7, 130.9°) show that this atom is sp^2-hybridized. The expected C−C−C bond angle of 120° for an unstrained system is widened by the coordinated lithium atom. Obviously, there is no electron density accumulated at the central carbon atom. The two pyridyl rings are only twisted with respect to each other by 5.6°, suggesting that the anion is fully conjugated. Above and below that plane, the lithium atom is additionally coordinated by two thf molecules.

Crystal Structure of 2. In hydrocarbons the lithiation of the bis(2-(pyridyl)methane can be stopped halfway. Half an equivalent is deprotonated, while the other half acts as a nitrogen donor base (Figure 2; Table

Table 1. Selected Bond Lengths (pm) and Angles (deg) of 1−6

1		2		3		4		5		6	
C1−C2	140.6(3)	C1−C2	139.1(7)	C1−C2	141.7(4)	C1−C2	138.9(4)	C1−C2	139.1(7)	C1−C2	138.8(5)
C1−C7	140.6(3)	C1−C7	141.0(6)	C1−C7	140.5(4)	C1−C7	141.2(4)	C1−C7	140.8(8)	C1−C7	140.3(5)
		C12−C13	149.2(7)	C12−C13	140.6(4)	C20−C21	140.6(4)				
		C12−C18	150.5(7)	C12−C18	141.2(4)	C20−C26	141.0(4)				
Li1−N1	196.6(4)	Li1−N1	196.0(9)	Li1−N1	201.5(5)	Li1−N1	201.0(5)	Al1−N1	190.8(4)	Ga1−N1	198.3(3)
Li1−N2	197.3(4)	Li1−N2	197.6(9)	Li1−N2	202.6(5)	Li1−N2	200.0(5)	Al1−N2	190.9(4)	Ga1−N2	197.9(3)
Li1−O1	199.4(4)	Li1−N3	207.1(9)	Li1−N3	200.1(5)	Li1−N3	200.4(5)	Al1−C12	195.3(6)	Ga1−C12	194.7(4)
Li1−O2	196.5(3)	Li1−N4	205.8(8)	Li1−N4	200.3(5)	Li1−N4	198.5(5)	Al1−C13	195.9(6)	Ga1−C13	195.9(4)
				Li2−O(av)	236.5	Na−O(av)	237.3				
C2−C1−C7	130.9(2)	C2−C1−C7	132.6(5)	C2−C1−C7	130.3(2)	C2−C1−C7	131.9(3)	C2−C1−C7	129.4(4)	C2−C1−C7	131.1(4)
		C13−C12−C18	115.0(4)	C13−C12−C18	130.8(2)	C21−C20−C26	130.4(2)				
N1−Li1−N2	96.4(2)	N1−Li1−N2	97.1(4)	N1−Li1−N2	92.6(2)	N1−Li1−N2	93.6(2)	N1−Al1−N2	97.1(1)	N1−Gal−N2	94.9(1)
N1−Li1−O1	118.6(2)	N1−Li1−N3	115.6(4)	N1−Li1−N3	126.8(2)	N1−Li1−N3	124.2(3)	N1−Al1−C12	109.7(4)	N1−Ga1−C12	109.1(2)
N1−Li1−O2	115.3(2)	N1−Li1−N4	110.6(4)	N1−Li1−N4	107.9(2)	N1−Li1−N4	112.7(2)	N1−Al1−C13	110.0(2)	N1−Ga1−C13	108.8(2)
N2−Li1−O1	106.5(2)	N2−Li1−N3	123.3(5)	N2−Li1−N3	115.5(2)	N2−Li1−N3	120.2(2)	N2−Al1−C12	110.2(2)	N2−Ga1−C12	108.8(2)
N2−Li1−O2	122.3(2)	N2−Li1−N4	117.7(4)	N2−Li1−N4	123.2(2)	N2−Li1−N4	113.5(2)	N2−Al1−C13	110.7(2)	N2−Gal−C13	109.9(2)
O1−Li1−O2	98.9(9)	N3−Li1−N4	93.5(3)	N3−Li1−N4	93.6(2)	N3−Li1−N4	94.0(2)	C12−Al1−C13	117.4(2)	C12−Ga1−C13	121.9(2)

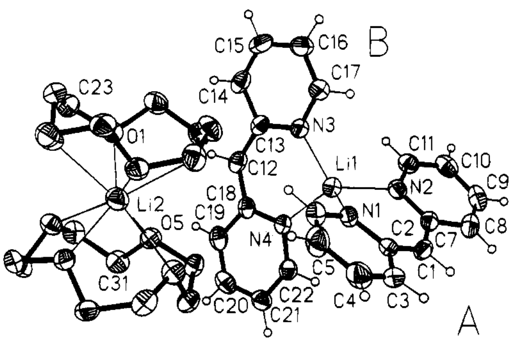

Figure 3. Crystal structure of **3**, anisotropic displacement parameters depicting 50% probability. The hydrogen atoms of both crown ether molecules have been omitted for clarity.

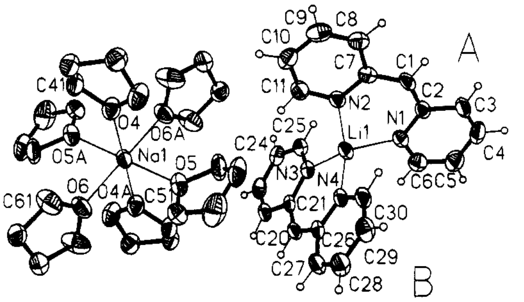

Figure 4. Crystal structure of **4**, anisotropic displacement parameters depicting 50% probability. The hydrogen atoms of the thf molecules coordinated to sodium and the single lattice THF molecule have been omitted for clarity.

1). The Li–N distances of the metal to the anion are significantly shorter (196.0 and 197.6 pm) than those to the intact starting material molecule (207.1 and 205.8 pm). Again, the anion is planar (mean deviation from the plane: 5.8 pm), but the lithium atom is 48.5 pm out of that plane. The two pyridyl rings are twisted by only 7.6°. The two central C–C bonds in the anion are in good agreement with the C–C distances in an aromatic system (139.1 and 141.0 pm). Furthermore, the position of the single hydrogen atom at C1 was taken from the difference map and refined freely.

The conformation of the donating bis(2-pyridyl)methane is quite different. Not only is the angle of the normals to the planes of the two pyridyl rings 124.5° but also the basic structural parameters of the central carbon atom indicate an sp^3-type atom. The C–C bonds are significantly longer (150.5 and 149.2 pm), hence in good accordance with a standard C(sp^3)–C(sp^2) single bond of 151 pm.[15] In addition, the C–C–C angle is more acute than that of the anion (115.0 compared to 132.6°). Again, the positions of the two hydrogen atoms at C12 were taken from the difference map and refined freely.

Crystal Structure of 3. **1** was reacted with 1 equiv of 12-crown-4 (eq 3), and in fact the presence of the crown ether removes the lithium atom 0.5 equiv of **1**, but the free anion is coordinated to the second half of **1**, removing the coordinated thf. Hence **1** reacts in the ratio 1:1 with crown ether to give the lithium lithiate **3**. Up to now, only two related structures of this type have been known.[16,17] A lithium atom coordinated to two neutral crown ether molecules gives the cation while the second lithium atom surrounded by two anions is part of the overall anion (Figure 3; Table 1).

The Li–N distances in **3** are almost exactly halfway between the short Li–N distances in the contact ion pairs of **1** and **2** and the long Li–N donor distances in **2**. The average value of 201.1 pm in **3** shows the steric demand of two (2-NC_5H_4)CH anions coordinated to a single lithium cation. These two anions are significantly different. Anion A (Figure 3) deviates considerably from planarity: the mean deviation from the plane is 12.4 pm, and the two pyridyl rings are twisted by 15.6°. Li1 is 73 pm out of the plane of anion A. B is similar to the anions in **1** and **2**: the mean deviation from the plane is only 5.0 pm, and the two pyridyl rings are only twisted by 6.1°. Li1 is only 15.5 pm out of the plane of the anion. The C1⋯Li1⋯C12 angle is 159.8°, and the planes of the anions are almost perpendicular (82.3°).

Crystal Structure of 4. Crystals of **4** were obtained at −35 °C from a THF solution. One of the low-melting single crystals (mp < −30 °C) was selected and transferred to the diffractometer at −80 °C.[18] To our knowledge **4** is the first example of a sodium lithiate, although a few mixed lithium/sodium metal organic complexes are known.[19] Formally, only the Li(12-crown-4)$_2$ cation in **3** is replaced by the Na(thf)$_6$ cation.[20]

The two anions coordinated to the lithium atom in **4** are not as different (Figure 4, Table 1) as in **3**. Both anions A and B are planar (mean deviation from the plane: 4.8 pm in A and 2.4 pm in B), and the two pyridyl rings are only slightly twisted (5.9° in A and 3.0° in B). While the lithium atom is 40.9 pm out of the plane of anion A, it is only 8.9 pm out of that of B. Both anions are almost orthogonal (88.3°) with respect to each other. The Li1⋯C1⋯C20 angle is 162.6°. The Li–N distances (average 200.0 pm) are very similar to those of **3**, hence located between an Li–N distance in a lithium amide and an Li–N donor bond.

Apparently, two (2-NC_5H_4)$_2$CH anions accommodate a single Li cation very well; therefore this structural motif is present in **3** and **4**. This might be the reason why total metal exchange does not occur.

In the mixture of RLi/NaO^{t}Bu,[21-23] the R^- does not necessarily have to be a "classical" carbanion like Me^- or Bu^-. With the right shape and basicity of the anion,

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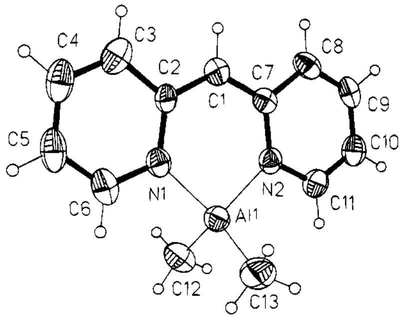


Figure 5. Crystal structure of **5**, anisotropic displacement parameters depicting 50% probability.

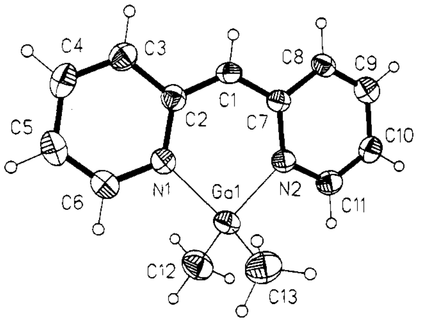


Figure 6. Crystal structure of **6**, anisotropic displacement parameters depicting 50% probability.

selective transmetalation can be achieved. The very strong Li−O interaction is often regarded as the driving force in this type of reaction. This now seems questionable, because in **4** only one Li−O bond instead of the possible two is formed. Obviously, two chelating $(2\text{-}NC_5H_4)_2CH$ anions are energetically more favorable than another Li−O bond. Even the relatively labile Na(thf)$_6$ cation is favored.

Crystal Structures of 5 and 6. In **5**, the $(thf)_2Li$ unit of **1** is formally replaced by an Me_2Al unit (Figure 5, Table 1), and by an Me_2Ga unit (Figure 6; Table 1) in **6**. **5** adopts an unusual monomeric structure in the solid state.[24−26] Like the alkali metals, the aluminum atom in **5** is chelated by the two nitrogen atoms within the pyridyl rings. It is only 1.1 pm out of the plane of the anion, whereas the methyl groups are located above and below that plane. Again, the anion is planar (mean deviation 0.8 pm) and the two pyridyl rings are only twisted by 0.8° with respect to each other. Hence, compared to the other anions discussed in this paper, that one in **5** fulfills the criterion of planarity almost ideally.

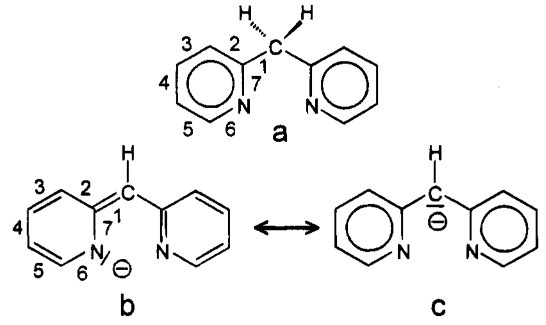
The Al−N bond lengths (Al1−N1, 190.8 pm; Al1−N2, 190.9 pm) are in good agreement with literature values;[24] the Al−C distances (Al1−C12, 195.3 pm; Al1−C13, 195.9 pm) are comparable with the distances in Me_3Al.[27−29]

The gallium atom in **6** is like the aluminum atom in **5**, coordinated to the ring nitrogen atoms. It is 29 pm out of the plane of the anion. The gallium atom fits the bite of the ligand not as perfect as the aluminum does. The mean deviation from planarity is 4.7 pm, and the two pyridyl rings are twisted by 5.5°. The slightly longer Ga−N bonds of 198.3 (N1) and 197.9 (N2) pm reflect the increase in the covalent radius of gallium compared with aluminum. In the $[GaN]_4$ heterocubane skeleton of $[NHC_6F_5Ga(MesGa)_3(\mu_3\text{-}NC_6F_5)_4]$[30] (Mes = $2,4,6\text{-}Me_3C_6H_2$), the Ga−N distances range from 196 to 206 pm. The Ga−C distances (Ga1−C12, 194.7 pm; Ga1−C13, 195.9 pm) are similar to the distances found in Me_3Ga in the gas phase.[31]

Structural Comparison

The outstanding common feature of all discussed structures is that the anion exclusively coordinates the metals *via* the two nitrogen atoms. Furthermore, all anions are more or less ideally planar.

Thus, the central deprotonated carbon atom is to be regarded as sp^2-hybridized without any negative charge being accumulated. Hence, the mesomeric form **c** is unsuitable for describing the anion in an adequate way. All experiments prove that **b** is the form which contributes most. The average bond lengths show that the double bonds are localized in positions 1, 3, and 5 (averages of sixteen equivalent bonds in eight anions). The N−C bonds are lengthened significantly, indicating accumulation of negative charge on nitrogen. Compared with the donating $(2\text{-}NC_5H_4)_2CH_2$ in **2** (depicted in **a**), the central C−C bond is considerably shortened by 10 pm. **A** shows delocalization within the aromatic system.



	1	2	3	4	5	6	7
a	149.9	138.0	137.5	137.2	137.1	133.1	134.8
b	140.4	142.7	135.6	139.1	136.3	134.9	136.8

The C−C bond between the central carbon atom and the ipso carbon atom of the alkali metal η^6-coordinated phenyl ring in $Ph_3CK\cdot pmdeta/thf$ (pmdeta = $MeN(CH_2CH_2NMe_2)_2$), $[Ph_3CRb\cdot pmdeta]_\infty$, and $[Ph_3CCs\cdot pmdeta]_\infty$[1] is shortened on average by 2.5 pm, while the one to the ipso carbon atom of the pyridyl ring in $Ph_2(2\text{-}NC_5H_4)CLi\cdot 2Et_2O$, $Ph_2(2\text{-}NC_5H_4)CNa\cdot 3thf$, and $Ph_2(2\text{-}NC_5H_4)$-

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Table 2. Crystal Data for 1−6

	1	**2**	**3**	**4**	**5**	**6**
formula	$C_{19}H_{25}LiN_2O_2$	$[C_{22}H_{19}LiN_4]C_7H_8$	$C_{38}H_{50}Li_2N_4O_8$	$C_{50}H_{74}LiN_4NaO_7$	$C_{13}H_{15}AlN_2$	$C_{13}H_{15}GaN_2$
fw	320.4	438.5	704.7	873.1	226.3	269.0
cryst syze (mm)	0.8 × 0.6 × 0.5	0.4 × 0.4 × 0.3	0.5 × 0.4 × 0.4	0.4 × 0.4 × 0.3	0.4 × 0.3 × 0.3	0.4 × 0.2 × 0.2
space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$Pca2_1$	$Pbcn$
a (pm)	970.4(1)	1395.8(3)	1194.1(6)	1132.4(5)	1281.7(1)	2715.1(5)
b (pm)	1305.3(1)	1251.3(4)	2404.9(12)	1407.3(7)	793.1(1)	705.3(1)
c (pm)	1354.5(3)	1420.5(3)	1320.8(7)	1788.5(9)	1227.8(1)	1321.4(3)
α (deg)	90	90	90	93.49(2)	90	90
β (deg)	90	95.85(3)	101.74(3)	106.73(2)	90	90
γ (deg)	90	90	90	112.76(2)	90	90
V (nm^3)	1.716(1)	2.468(1)	3.714(3)	2.469(2)	1.248(1)	2.530(1)
Z	4	4	4	2	4	8
temp (K)	153(2)	153(2)	153(2)	153(2)	193(1)	153(2)
ϱ_c (Mg m^{-3})	1.240	1.180	1.260	1.175	1.204	1.412
μ (mm^{-1})	0.079	0.070	0.087	0.085	0.137	2.149
F(000)	688	928	1504	944	480	1104
2θ range (deg)	8−55	8−45	8−50	8−45	8−50	8−55
no. of reflns measd	3712	3520	7744	8151	4209	4219
no. of unique reflns	3264	3198	6512	6405	2214	2924
no. of restraints	120	377	25	709	1	0
refined param	317	386	541	688	149	150
$R1$ [$I > 2\sigma(I)$]	0.0398	0.0684	0.0502	0.0554	0.0584	0.0471
$wR2^a$ (all data)	0.1523	0.1891	0.1591	0.1554	0.1601	0.1169
$g1$; $g2^b$	0.035; 0.383	0.050; 3.930	0.050; 1.070	0.078; 1.933	0.090; 0.000	0.049; 0.335
highest diff peak (10^{-6} e pm^{-3})	0.13	0.27	0.20	0.37	0.70	0.51

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

CK·pmdeta/thf is shortened by 5.5 pm. The bond shortening in **1**−**6** is even more pronounced, possibly because of the missing third aromatic ring at the central carbon atom.

However, the anions in **1**−**6** are considered to be amides. The coordination behavior of those amides seems to be quite rigid. Because they are fully conjugated, the N−N distance varies only between 286.1 (**5**) and 294.9 (**2**) pm. Thus they are comparable with other chelating amides like $Me_2Si(N^tBu)^{2-}$,[32] $PhC(NSiMe_3)_2^-$,[33] $RS(NR)_2^-$,[34] and $Ph_2P(NSiMe_3)_2^-$.[20c] The bite of these ligands is not tunable to the metal. Varying the bite is achieved by using the heavier homologues of carbon like germanium and tin as the central atom between pyridyl or pyrazolyl rings.[35]

Conclusion

The alkali metals coordinated to the triphenylmethyl carbanion shift from the central carbon atom to the η^6-coordination of a ring as they become heavier. In the diphenylpyridylmethyl carbanion, the negative charge is almost entirely located on the nitrogen ring atom. The bis(pyridyl)methyl anions discussed here form amides, with nearly ideal coplanar pyridyl rings. Two amides surrounding a lithium atom seem energetically favorable, stabilizing a lithium lithiate and a sodium lithiate. The two group 13 metals aluminum and gallium are coordinated in the same way as the alkali metals. The very similar radii of lithium, aluminum, and gallium match the bite of the ligand very well. The bigger sodium is not coordinated to the bis(pyridyl)methyl anion.

Experimental Section

All manipulations were performed under an inert atmosphere of dry nitrogen gas 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 benzene-d_6, toluene-d_8, or THF-d_8 with $SiMe_4$, LiCl, and NaCl as external standards. EI mass spectra were measured on Finnigan MAT 8230 or Varian MAT CH 5 instruments. Elemental analyses were obtained from the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen.

1: 0.68 g (4 mmol) of $H_2C(2\text{-}NC_5H_4)_2$ in 25 mL of THF was reacted with the equimolar amount of ^{n}BuLi (1.74 mL of a 2.3 M solution) at −80 °C. Evaporating off the solvent gives an orange precipitate, which was washed twice with 10 mL of pentane. Crystallization from THF yielded crystals suitable for X-ray diffraction. Yield: 0.47 g; 67%. Mp: 40 °C; decomposition at $T \geq 70$ °C. ^{1}H NMR (THF-d_8, room temperature): δ 1.77, 3.58 (thf), 4.63 (s, H1), 5.80 (ddd, $^3J_{5,4}$ 6.61, $^3J_{5,6}$ 5.31, $^4J_{5,3}$ 1.11 Hz, H5), 6.28 (ddd, $^3J_{3,4}$ 8.65, $^4J_{3,5}$ 1.11, $^4J_{3,1}$ 1.11 Hz, H3), 6.74 (ddd, $^3J_{4,3}$ 8.65, $^3J_{4,5}$ 6.61, $^4J_{4,6}$ 1.91 Hz, H4), 7.59 (dd, $^3J_{6,5}$ 5.31, $^4J_{6,4}$ 1.91 Hz, H6). ^{13}C NMR (THF/C_6D_6, room temperature) δ 88.4 (s, C1), 110.7 (s, C5), 122.8 (s, C3), 135.6 (s, C4), 141.2 (s, C6), 155.1 (s, C2). ^{7}Li NMR (THF-d_8, room temperature): δ 3.25. MS (70 eV): m/z (%) 169 (100) ($CH(2\text{-}NC_5H_4)_2$), 85 (8) ($Li2\text{-}NC_5H_4$), 78 (8) ($2\text{-}NC_5H_4$). Anal. Calcd (found): C, 71.23 (68.86); H, 7.86 (7.73), N, 8.74 (8.27).

2 was synthesized like **1** at −80 °C, using toluene instead of THF as solvent. The reaction mixture was immediately transferred to a deep freeze (−100 °C). After 5 days, colorless crystals, suitable for X-ray structure analysis, were obtained. The crystals decompose at temperatures slightly higher than

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Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (pm^2 × 10^{-1}) for 1

	x	*y*	*z*	*U*(eq)^a
C1	3385(2)	8505(2)	7507(2)	34(1)
C2	2793(2)	7869(1)	6785(1)	30(1)
C3	3665(2)	7309(2)	6131(2)	39(1)
C4	3152(3)	6703(2)	5410(2)	41(1)
C5	1737(2)	6619(2)	5309(2)	39(1)
C6	934(2)	7158(1)	5949(2)	34(1)
N1	1398(2)	7770(1)	6673(1)	30(1)
C7	2778(2)	9096(1)	8258(1)	32(1)
C8	3634(2)	9712(2)	8873(2)	40(1)
C9	3097(3)	10290(2)	9605(2)	44(2)
C10	1686(3)	10291(2)	9760(2)	42(2)
C11	904(2)	9694(2)	9153(2)	38(1)
N2	1390(2)	9108(1)	8416(1)	32(1)
Li1	41(3)	8421(2)	7550(3)	34(2)
O1	−1166(1)	9518(1)	7002(1)	37(1)
C12	−2554(3)	9797(2)	7208(2)	52(1)
C13	−2887(3)	10688(2)	6527(2)	56(2)
C14	−1516(3)	11003(2)	6106(2)	57(2)
C15	−499(2)	10459(2)	6750(2)	43(1)
O2	−1394(1)	7505(1)	8069(1)	37(1)
C16	−2339(2)	6945(2)	7445(2)	38(1)
C17	−3432(3)	6523(2)	8110(2)	49(2)
C18	−3427(2)	7261(2)	8974(2)	46(1)
C19	−1934(3)	7523(2)	9059(2)	48(1)

^{a} *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (pm^2 × 10^{-1}) for 2

	x	*y*	*z*	*U*(eq)^a
Li1	6363(6)	1427(7)	7145(5)	45(2)
C1	5612(4)	−49(4)	8734(3)	37(1)
C2	6582(4)	−211(4)	8627(3)	37(1)
C3	7105(4)	−1022(4)	9144(3)	45(1)
C4	8052(5)	−1174(4)	9092(4)	56(2)
C5	8540(4)	−510(5)	8499(4)	61(2)
C6	8004(4)	241(5)	7990(4)	55(2)
N1	7055(3)	424(3)	8030(2)	40(1)
C7	4945(3)	735(4)	8380(3)	32(1)
C8	4002(4)	718(4)	8679(3)	41(1)
C9	3343(4)	1466(4)	8379(3)	46(1)
C10	3584(4)	2279(4)	7779(3)	45(1)
C11	4499(4)	2266(4)	7517(3)	42(1)
N2	5177(3)	1522(3)	7790(2)	37(1)
C12	6220(4)	2660(4)	5246(4)	45(1)
C13	7059(4)	3068(4)	5880(3)	40(1)
C14	7706(4)	3768(4)	5546(3)	43(1)
C15	8452(4)	4172(4)	6153(4)	53(2)
C16	8547(4)	3842(4)	7081(4)	54(2)
C17	7883(4)	3137(4)	7362(4)	51(2)
N3	7142(3)	2751(3)	6792(3)	42(1)
C18	6243(3)	1482(4)	5039(3)	39(1)
C19	6250(4)	1090(5)	4130(3)	49(1)
C20	6255(4)	8(5)	3982(4)	57(2)
C21	6256(4)	−664(4)	4741(4)	54(2)
C22	6253(4)	−217(4)	5626(4)	47(1)
N4	6247(3)	823(3)	5791(2)	39(1)

^{a} *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$j tensor.

−50 °C, so one crystal was transferred to the diffractometer at ca. −60 °C.[18] Because of the high sensitivity of **2**, no other spectroscopic or analytical data could be obtained.

Table 5. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (pm^2 × 10^{-1}) for 3

	x	*y*	*z*	*U*(eq)^a
Li1	2651(3)	3853(2)	8328(3)	37(2)
C1	2574(2)	3292(1)	10566(2)	33(1)
C2	2702(2)	3878(1)	10604(2)	31(1)
C3	2659(2)	4166(1)	11533(2)	39(1)
C4	2811(3)	4725(1)	11608(2)	50(2)
C5	3014(3)	5023(1)	10761(2)	53(2)
C6	3042(2)	4730(1)	9879(2)	41(2)
N1	2885(2)	4176(1)	9764(1)	32(1)
C7	2767(2)	2908(1)	9819(2)	32(1)
C8	2791(2)	2327(1)	10054(2)	40(1)
C9	3082(2)	1943(1)	9397(2)	46(1)
C10	3333(2)	2118(1)	8459(2)	44(1)
C11	3250(2)	2676(1)	8243(2)	38(1)
N2	2967(2)	3068(1)	8873(2)	33(1)
C12	1748(2)	4369(1)	5976(2)	36(2)
C13	2936(2)	4289(1)	6259(2)	33(2)
C14	3641(3)	4444(1)	5548(2)	42(2)
C15	4799(3)	4385(1)	5797(2)	50(2)
C16	5309(2)	4171(1)	6760(3)	52(2)
C17	4598(2)	4027(1)	7408(2)	45(2)
N3	3456(2)	4077(1)	7204(2)	34(1)
C18	877(2)	4292(1)	6543(2)	32(1)
C19	−284(2)	4419(1)	6088(2)	40(2)
C20	−1131(2)	4361(1)	6628(2)	43(1)
C21	−869(2)	4180(1)	7655(2)	40(1)
C22	258(2)	4062(1)	8056(2)	33(1)
N4	1118(2)	4102(1)	7544(1)	30(1)
Li2	2048(4)	6629(2)	7873(4)	41(2)
O1	2648(1)	6337(1)	6300(1)	43(1)
C23	2925(2)	6809(1)	5740(2)	47(2)
C24	3617(2)	7222(1)	6454(2)	47(2)
O2	2980(1)	7377(1)	7208(1)	40(1)
C25	3626(2)	7686(1)	8053(2)	43(1)
C26	4357(2)	7315(1)	8831(2)	41(1)
O3	3618(1)	6920(1)	9158(1)	35(1)
C27	4202(2)	6439(1)	9640(2)	42(1)
C28	4377(2)	6021(1)	8847(2)	44(1)
O4	3276(1)	5893(1)	8241(1)	35(1)
C29	3319(2)	5566(1)	7343(2)	40(2)
C30	3516(2)	5923(1)	6467(2)	48(2)
O5	788(1)	5945(1)	7484(1)	36(1)
C31	−280(2)	6081(1)	6841(2)	39(1)
C32	−43(2)	6504(1)	6070(2)	37(1)
O6	536(1)	6978(1)	6584(1)	35(1)
C33	−200(2)	7362(1)	6957(2)	38(1)
C34	543(2)	7705(1)	7784(2)	35(1)
O7	1157(1)	7358(1)	8589(1)	32(1)
C35	504(2)	7199(1)	9332(2)	37(1)
C36	1186(2)	6781(1)	10043(2)	39(2)
O8	1442(1)	6401(1)	9495(1)	37(1)
C37	515(2)	5916(1)	9246(2)	37(1)
C38	694(2)	5588(1)	8330(2)	36(1)

^{a} *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

3: 1.7 g (10 mmol) of $H_2C(2\text{-}NC_5H_4)_2$ in 30 mL of hexane was reacted with 5.4 mL of ^{n}BuLi (1.85 M solution) at −80 °C. After stirring for 2 h, 2.0 g (11.3 mmol) of 12-crown-4 was added. The reaction mixture was warmed to room temperature, and the precipitate was redissolved by a small amount of THF. Storage at −35 °C yielded single crystals suitable for X-ray diffraction. Yield: 3 g, 85%. Mp: 193 °C; decomposition at $T \geq 215$ °C. **3** is insoluble in hydrocarbons, and NMR investigations in THF show chemical shifts similar to those of **1**. ^{6}Li CP/MAS NMR ($^6LiCO_3$ external standard): δ −2.5 (Li2; see Figure 3) and 3.3 (Li1; see Figure 3). MS (70 eV): *m/z* (%) 169 (100) ($CH(2\text{-}NC_5H_4)_2$).

4: 0.77 g (8 mmol) of NaO^{t}Bu and 1.40 g (8 mmol) of $Li(2\text{-}NC_5H_4)_2CH$ were stirred in 30 mL of THF at room temperature. The reaction mixture was directly transferred to a deep freeze. After 3 days at −35 °C, colorless crystals were obtained. Mp: ca. −30 °C. All NMR data were obtained from the vacuum-dried THF-free powder (decomposition $T > 270$ °C). ^{1}H NMR (THF-d_8, room temperature): δ 4.61 (s, H1), 5.70 (ddd, $^3J_{5,4}$ 6.55, $^3J_{5,6}$ 5.30, $^4J_{5,3}$ 1.1 Hz, H5), 6.23 (d, $^3J_{3,4}$ 8.60 Hz, H3), 6.69 (ddd, $^3J_{4,3}$ 8.60, $^3J_{4,5}$ 6.55, $^4J_{4,6}$ 1.99 Hz, H4), 7.59 (dd, $^3J_{6,5}$ 5.30, $^4J_{6,4}$ 1.99 Hz, H6). ^{13}C NMR (THF-d_8, room temperature): δ 87.8 (s, C1), 105.9 (s, C5), 120.1 (s, C3), 132.8 (s, C4), 148.1 (s, C6), 160.2 (s, C2). ^{7}Li NMR (THF-d_8, room temperature): δ 2.34 (s). ^{23}Na NMR (THF-d_8, room temperature): δ −0.49 (s, br). MS (70 eV): *m/z* (%) 368 (10) (M^+ − thf), 169 (100) ($CH(2\text{-}NC_5H_4)_2$), 79 (30) ($2\text{-}NC_5H_5$). Anal. Calcd for $[Na(thf)_3][Li\{(2\text{-}NC_5H_4)_2CH\}_2]$ (found): C, 69.78

Table 6. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for 4

	x	*y*	*z*	*U*(eq)[a]
Li1	3005(5)	1434(4)	1947(3)	37(1)
C1	4761(3)	381(2)	1333(2)	36(1)
C2	4356(3)	−25(2)	1952(2)	35(1)
C(3)	4790(3)	−783(2)	2294(2)	47(1)
C4	4402(3)	−1202(3)	2891(2)	54(1)
C5	3577(4)	−891(3)	3190(2)	54(1)
C6	3189(3)	−171(2)	2847(2)	46(1)
N1	3543(2)	271(2)	2254(1)	36(1)
C7	4414(3)	1061(2)	856(2)	34(1)
C8	4963(3)	1330(2)	242(2)	41(1)
C9	4619(3)	1960(3)	−241(2)	50(1)
C10	3715(3)	2354(2)	−124(2)	48(1)
C11	3229(3)	2084(2)	480(2)	43(1)
N2	3545(2)	1468(2)	975(1)	34(1)
C20	2167(3)	3019(2)	2902(2)	33(1)
C21	1060(3)	2167(2)	2343(2)	29(1)
C22	−291(3)	2061(2)	2239(2)	35(1)
C23	−1393(3)	1269(2)	1706(2)	41(1)
C24	−1224(3)	541(2)	1242(2)	41(1)
C25	83(3)	663(2)	1359(2)	38(1)
N3	1212(2)	1439(2)	1887(1)	32(1)
C26	3578(3)	3325(2)	3101(2)	31(1)
C27	4510(3)	4257(2)	3676(2)	42(1)
C28	5878(3)	4575(2)	3872(2)	50(1)
C29	6372(3)	3986(2)	3513(2)	49(1)
C30	5440(3)	3102(2)	2966(2)	40(1)
N4	4086(2)	2758(2)	2753(1)	32(1)
Na1	0	5000	0	38(1)
O4	1287(2)	5422(2)	−863(1)	48(1)
C41	862(3)	5734(3)	−1598(2)	49(1)
C42	2117(3)	6302(3)	−1796(2)	47(1)
C43	2980(3)	5736(3)	−1455(2)	54(1)
C44	2598(3)	5432(3)	−738(2)	59(1)
O5	1943(2)	5076(2)	1034(1)	52(1)
C51	2984(12)	5992(7)	1568(8)	49(3)
C52	4220(11)	5825(11)	1855(8)	83(5)
C53	3912(11)	4773(14)	1406(18)	65(5)
C54	2402(4)	4260(3)	1093(2)	65(1)
O6	693(2)	6792(2)	540(1)	55(1)
C61	1295(4)	7704(3)	232(3)	72(1)
C62	837(3)	8491(2)	486(2)	50(1)
C63	243(4)	8070(3)	1120(2)	57(1)
C64	114(20)	7009(11)	1077(11)	74(7)
Na2	0	0	5000	32(1)
O7	1237(2)	−1025(2)	5447(1)	43(1)
C71	2605(3)	−794(3)	5484(2)	50(1)
C72	3025(3)	−1554(3)	5922(2)	48(1)
C73	2072(3)	−1904(3)	6381(1)	51(1)
C74	785(3)	−1883(2)	5828(2)	43(1)
O8	534(2)	859(2)	6311(1)	43(1)
C81	1187(5)	609(3)	7027(2)	73(1)
C82	2092(4)	1627(3)	7594(2)	60(1)
C83	1527(3)	2390(2)	7279(2)	50(1)
C84	307(3)	1731(2)	6564(2)	47(1)
O(9)	1954(2)	1356(2)	4928(1)	45(1)
C91	2850(11)	2238(8)	5547(6)	53(3)
C92	4093(3)	2793(3)	5335(2)	64(1)
C93	4080(3)	1945(3)	4769(2)	54(1)
C94	2581(3)	1265(2)	4357(2)	45(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

(62.54); H, 7.24 (6.56); N, 9.58 (9.77). This approximation suggests that THF might not leave the crystals in a stoichiometric amount when they are taken out of the mother liquor at low temperatures.

5 can be synthesized in two different ways. Firstly, 0.17 g (1 mmol) of $H_2C(2\text{-}NC_5H_4)_2$ in 20 mL of diethyl ether was reacted with 0.44 mL of ^{n}BuLi (2.3 M solution) at −80 °C and warmed to −50 °C. After stirring for 1 h, 1 mL of a 1 M solution of Me_2AlCl in hexane was added, and the former pale yellow solution turned orange. It was then warmed to room temperature, stirred for 12 h, and filtered through a glass frit. Half the amount of solvent was evaporated off. Storage of the clear solution at −35 °C yielded orange crystals. In the second route, 0.68 g (4 mmol) of $H_2C(2\text{-}NC_5H_4)_2$ in 20 mL of diethyl ether was reacted at −50 °C with 2 mL of a 2 M solution of Me_3Al in hexane. The reaction mixture was warmed to room temperature and stirred for 5 h. After evaporating off the solvent, the precipitate was washed twice with 10 mL of hexane. The reaction yielded 0.22 g, 25%, of pure product. Mp: 85 °C. ^{1}H NMR (C_6D_6, room temperature): δ −0.32 (s, Me), 4.91 (s, H1), 5.79 (ddd, $^3J_{5,4}$ 6.68, $^3J_{5,6}$ 6.16, $^4J_{5,3}$ 1.14 Hz, H5), 6.30 (ddd, $^3J_{3,4}$ 8.85, $^4J_{3,5}$ 1.14, $^4J_{3,1}$ 1.14 Hz, H3), 6.55 (ddd, $^3J_{4,3}$ 8.85, $^3J_{4,5}$ 6.68, $^4J_{4,6}$ 1.6 Hz, H4), 7.27 (dd, $^3J_{6,5}$ 6.16 Hz, H6). ^{13}C NMR (THF, C_6D_6, room temperature): δ 87.6 (s, C1), 106.0 (s, C5), 120.3 (s, C3), 132.7 (s, C4), 146.5 (s, C6), 159.0 (s, C2). Anal. Calcd (found): C, 69.01 (65.08); H, 6.68 (7.08); N, 12.38 (10.63).

Table 7. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for 5

	x	*y*	*z*	*U*(eq)[a]
Al1	1252(1)	1718(1)	4775(2)	35(1)
C1	1207(4)	5767(5)	4850(5)	37(2)
N1	2186(3)	3359(5)	4192(3)	34(2)
C2	2051(4)	5063(6)	4301(4)	30(3)
C3	2816(4)	6167(7)	3836(4)	44(3)
C4	3647(5)	5538(9)	3285(4)	48(3)
C5	3758(5)	3800(8)	3195(4)	49(3)
C6	3024(4)	2787(7)	3648(4)	42(3)
N2	294(3)	3261(5)	5426(3)	33(2)
C7	375(5)	4963(5)	5389(5)	29(3)
C8	−404(4)	5954(7)	5921(4)	40(3)
C9	−1219(5)	5170(6)	6444(4)	38(3)
C10	−1292(5)	3446(6)	6472(4)	44(3)
C11	−536(4)	2529(7)	5954(4)	39(3)
C12	1960(5)	407(7)	5900(5)	54(4)
C13	581(5)	470(7)	3590(5)	56(4)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

6: A solution of 1.42 g (10.5 mmol) of Me_2GaCl in 30 mL of toluene was added to a solution of 1.85 g (10.5 mmol) of $Li(2\text{-}NC_5H_4)_2CH$ in 30 mL of toluene at −80 °C. To complete the reaction, the mixture was stirred for 12 h at room temperature. The toluene was removed in vacuum, and the orange precipitate was redissolved in 20 mL of hexane. The resulting solution was filtered and storred at −35 °C. After 2 days orange crystals were obtained, suitable for X-ray structure analysis. Yield: 0.25 g, 8.8%. Mp: 72 °C. ^{1}H NMR (C_6D_6, room temperature): δ −0.52 (s, Me), 4.86 (s, H1), 5.80 (ddd, $^3J_{5,4}$ 6.71, $^3J_{5,6}$ 6.02, $^4J_{5,3}$ 1.25 Hz, H5), 6.30 (dddd, $^3J_{3,4}$ 8.78, $^4J_{3,5}$ 1.25, $^3J_{3,6}$ 0.93, $^4J_{3,1}$ 0.28 Hz, H3), 6.57 (dddd, $^3J_{4,3}$ 8.78, $^3J_{4,5}$ 6.71, $^4J_{4,6}$ 1.70, $^5J_{4,1}$ 0.11 Hz, H4), 7.06 (dddd, $^3J_{5,6}$ 6.02, $^4J_{6,4}$ 1.70, $^5J_{6,3}$ 0.93, $^5J_{6,1}$ 0.52 Hz, H6). ^{13}C NMR (C_6D_6, room temperature): δ −8.0 (s, Me), 88.0 (s, C1), 110.2 (s, C5), 122.3 (s, C3), 134.9 (s, C4), 142.0 (s, C6), 155.2 (s, C2). MS (70 eV): *m/z* (%) 268 (8) (M^+), 253 (16) ($M^+ - Me$), 238 (10) ($M^+ - 2Me$), 169 (100) ($CH(2\text{-}NC_5H_4)_2$), 99 (14) ($GaMe_2$), 69 (10) (Ga). Anal. Calcd (found): C, 58.05 (57.17); H, 5.62 (5.71); N, 10.41 (9.80).

X-ray Measurements of 1−6. Crystal data for the six structures are presented in Table 2. All data were collected at low temperatures using an oil-coated shock-cooled crystal[18] on a Stoe-Siemens AED with Mo Kα (λ = 71.073 pm) radiation. The structures were solved by direct methods using SHELXS-90[36] and refined with all data on F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (g1 \cdot P)^2 + g2 \cdot P$ with $P = (F_o^2 + 2F_c^2)/3$ using SHELXL-93.[37] In **1** the positions of the hydrogen atoms of the anion were refined freely, whereas only the C−H distances in the two thf molecules were restrained to be equal. In **2** a disordered toluene molecule is present in the lattice. It was refined by restraining the ADP's of neighboring atoms to be

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(36) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(37) Sheldrick, G. M. SHELXL-93, program for crystal structure refinement, University of Göttingen, 1993.

Table 8. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for 6

	x	*y*	*z*	*U*(eq)[a]
Ga1	3483(1)	5565(1)	5805(1)	32(1)
C1	4427(1)	8174(6)	6413(3)	31(1)
C2	4035(1)	8301(6)	7085(3)	31(1)
C3	4081(2)	9392(6)	7991(3)	35(1)
C4	3704(2)	9558(6)	8652(3)	44(1)
C5	3258(2)	8628(7)	8456(3)	51(1)
C6	3225(2)	7592(6)	7607(3)	45(1)
N1	3597(1)	7377(5)	6929(2)	35(1)
C7	4465(1)	7302(5)	5462(3)	27(1)
C8	4902(1)	7535(5)	4874(3)	31(1)
C9	4947(2)	6726(5)	3947(3)	35(1)
C10	4560(2)	5614(6)	3562(3)	35(1)
C11	4152(1)	5415(6)	4142(3)	35(1)
N2	4095(1)	6218(5)	5070(2)	29(1)
C12	2920(1)	6416(7)	5012(4)	51(1)
C13	3527(2)	2977(6)	6336(4)	50(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

similar. In **3** the C–H distances of the two anions were restrained to be equal. The hydrogen atoms of the crown ether molecules were geometrically idealized and refined using a riding model. In **4**, three of the six coordinated thf molecules are disordered. The disorder was refined by using similar restraints. It seems worth noting that the uncoordinated THF molecule in the asymmetric unit is not disordered at all. Selected bond lengths and angles of **1**–**6** can be found in Table 1, relevant crystallographic data for **1**–**6** are in Table 2, and fractional coordinates of **1**–**6** are presented in Tables 3–8.

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Supplementary Material Available: Tables of crystal data, fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates of **1**–**6** and fully labeled figures of 50% anisotropic displacement parameters of the structures **1**–**6** (84 pages). Ordering information is given on any current masthead page.

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