

Bis(tetramethylpiperidino)aluminum Halide Adducts $\text{tmp}_2\text{AlX} \cdot \text{Do}$ and Tetrahaloaluminates of Tricoordinated Aluminum Cations $[\text{tmp}_2\text{Al}(\text{Do})]\text{AlX}_4$

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Upon treatment with Lewis bases Do (Do = pyridine bases or THF), the Lewis acids tmp_2AlX (X = Cl, Br, I) are converted exclusively to the monoadducts $\text{tmp}_2\text{AlX} \cdot \text{Do}$ (**2–4**). The Al–X bonds of these addition compounds are considerably elongated, indicating a tendency towards the formation of ionic species $[\text{tmp}_2\text{Al}(\text{Do})]\text{X}$. Due to the steric requirements of the bulky tmp ligands, addition of an excess of the Lewis base does not force these compounds to form tetracoordinated aluminum cations $[\text{tmp}_2\text{Al}(\text{Do})_2]^+$ or pentacoordinated adducts $\text{tmp}_2\text{AlX} \cdot \text{Do}_2$. Attempts to prepare ionic representatives by reaction of $\text{tmp}_2\text{AlX} \cdot \text{Do}$ with “ate” complexes of comparatively low nucleophilicity [MY = NaBPh_4 , AgBPh_4 , $\text{LiB}(\text{C}_6\text{F}_5)_4$, AgBF_4 , AgOtos] result in phenylation products [e.g. tmp_2AlPh (**5a**) and $\text{BPh}_3 \cdot \text{py}$ (**5b**)] or tetracoordinated addition compounds $\text{tmp}_2\text{AlY} \cdot \text{Do}$ (Y = anion). However, addition of one equivalent of AlX_3 (X = Br, I) initiates halide abstraction with formation of the ionic $[\text{tmp}_2\text{Al}(\text{Do})]\text{AlX}_4$ species **6a–f**, as indicated by ^{27}Al -NMR

data and conductivity measurements. Solid $[\text{tmp}_2\text{Al}(\text{py})]\text{AlI}_4$ (**6b**) decomposes readily into tmpAlI_2 and $\text{tmpAlI}_2 \cdot \text{py}$ (**7c**). Addition of non-polar aliphatic solvents to solutions of $[\text{tmp}_2\text{Al}(\text{Do})]\text{AlX}_4$ (**6**) leads to slow decomposition into tmp_2AlX and $\text{AlX}_3 \cdot \text{Do}$ (**7a–b**, **d**). This also occurs in polar donor solvents, where compounds $\text{AlX}_3 \cdot \text{Do}$ are favoured due to the formation of penta- or hexacoordinated species $\text{AlX}_3 \cdot \text{Do} \cdot \text{Solv}_n$ ($n = 1, 2$). Semiempirical AM1 calculations reveal the gas-phase stability of the tricoordinated bis(tmp)aluminum cation in the salt $[\text{tmp}_2\text{AlPy}]\text{AlCl}_4$ as the only representative in a series of calculated aluminum cations $[(\text{R}_2\text{N})_2\text{AlPy}]\text{AlCl}_4$ ($\text{R}_2\text{N} = \text{Me}_2\text{N}$, Et_2N , $i\text{Pr}_2\text{N}$, tmp). According to these calculations, the stability of a given cation increases when tetrachloroaluminate is replaced by tetraiodoaluminate. Ab initio calculations have been performed on two cations $[(\text{H}_2\text{N})_2\text{Al}(\text{Do})]^+$ (Do = NH_3 , py) and indicate very short Al–N bond lengths owing to ionic bonding contributions.

As aluminum compounds exhibit the highest Lewis acidity amongst main group III species^{[3][4]}, tetra-, penta- and hexacoordinated Lewis acid–base complexes with many different neutral donor molecules have been described in the literature^[5]. Due to their importance in industrial processes^[6], complexes involving AlCl_3 and trimethylaluminum as Lewis acids [e.g. $\text{AlCl}_3 \cdot \text{NMe}_3$, $\text{AlCl}_3 \cdot (\text{NMe}_3)_2$, $\text{AlBr}_3 \cdot \text{diglyme}$ (diglyme = diethylene glycol dimethyl ether), $\text{AlMe}_3 \cdot \text{OMe}_3$, etc.]^{[4][7][8]} have been particularly well studied. These addition compounds can exist as covalent molecules or as ion pairs, as shown by X-ray crystal structure determinations [e.g. $[\text{AlCl}_2(\text{py})_4][\text{AlCl}_4]$ ^[3], ^{27}Al -NMR and conductivity measurements, e.g. of solutions of AlCl_3 or AlBr_3 in THF, diglyme, DME etc.^{[8][9]}. A fine example of this feature has recently been published by Atwood et al.^[10]. They investigated reactions of Me_2AlX (X = Cl, Br, I) with $t\text{BuNH}_2$ as a donor molecule. Whereas the chloride gave the molecular adduct $\text{Me}_2\text{AlCl} \cdot \text{NH}_2t\text{Bu}$, the bromide and iodide were forced to dissociate upon addition of excess $t\text{BuNH}_2$, forming the salts $[\text{Me}_2\text{Al}(\text{NH}_2t\text{Bu})_2]\text{X}$ (X = Br, I). The chemistry of tetracoordinated aluminum cations has so far been explored only fleetingly, and apart from the latter compounds, as far as we are aware, only two other spec-

ies of this type have been reported, namely $[t\text{Bu}_2\text{Al}(\text{tmeda})]^+$ by Uhl^[11] and **A** by Raston^[12].



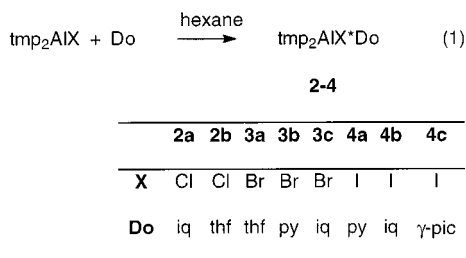
To the best of our knowledge, tricoordinated aluminum cations $[\text{R}_2\text{Al}(\text{Do})]^+$ (Do = monofunctional ligand) have yet to be observed and characterized.

In contrast to the aminoboron halides, aminoaluminum halides can be expected to be sufficiently acidic to form addition compounds [see $(\text{Me}_3\text{Si})_2\text{NAl}(\text{H})(\text{Cl}) \cdot \text{NMe}_3$ ^[13]. Even aminoorganylalanes form Lewis acid–base adducts, as exemplified by $\text{Ph}_2\text{NAlMe}_2 \cdot \text{NMe}_3$ and $\text{Ph}_2\text{NAlMe}_2 \cdot \text{OEt}_2$ ^[14]. Thus, the question arose as to whether the recently synthesized series of monomeric bis(amino)aluminum halides, tmp_2AlX (tmp = 2,2,6,6-tetramethylpiperidino, X = Cl **1a**, Br **1b**, I **1c**)^[15] and some products of nucleophilic substitution derived from these^{[16][17]} would still show

Lewis acidity. This was indeed found to be the case for **1a–c**. Here, we report on the addition compounds $\text{tmp}_2\text{AlX} \cdot \text{Do}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) as well as the salts $[\text{tmp}_2\text{Al}(\text{Do})]\text{Y}$ ($\text{Y} = \text{AlI}_4$).

Synthesis and Reactions

Addition of one equivalent of a donor molecule Do to *n*-hexane solutions of tmp_2AlX , **1a–c**, leads to immediate precipitation of the adducts $\text{tmp}_2\text{AlX} \cdot \text{Do}$ **2a, b, 3a–c**, and **4a–c** in almost quantitative yield, according to Eq. 1.

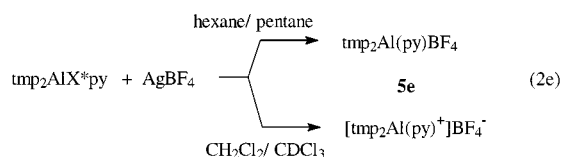
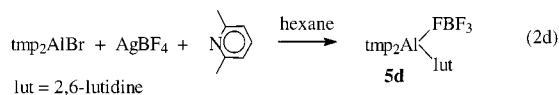
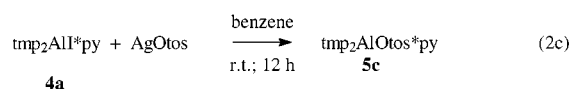
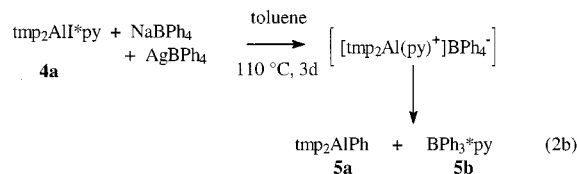
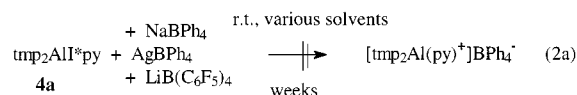


The adducts **2–4** are stable in vacuo and do not lose their donor molecules, even when subjected to high vacuum conditions at 50 °C. On the other hand, Et_2O , $t\text{BuPH}_2$, NEt_3 , and acridine do not give stable addition compounds (with respect to the application of vacuum). Moreover, tmp_2AlI (**1c**), the most Lewis acidic compound in the series of the halides **1a–c**, crystallizes from Et_2O as its tricoordinated monomer, as proven by NMR and by examination of its unit cell parameters^[15]. Compounds **2–4** are readily soluble in aromatic hydrocarbons, CH_2Cl_2 , CH_2Br_2 , THF, and Et_2O . Addition of a large excess of donor (up to ten-fold, or, in the case of THF, using the donor as solvent) does not force coordination of a further donor molecule (i.e. bring about pentacoordination at the aluminum atom), nor does it induce dissociation into ionic $[\text{tmp}_2\text{Al}(\text{Do})_2]\text{X}$ species. The addition compounds **2–4** can be crystallized from THF and no replacement of Do by the solvent is observed.

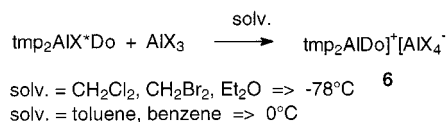
Attempts to prepare low coordinated ionic species of the type $[\text{tmp}_2\text{Al}(\text{py})]\text{Y}$ ($\text{Y} = \text{anion}$) by addition of NaBPh_4 , AgBPh_4 , or $\text{LiB}(\text{C}_6\text{F}_5)_4$ to solutions of $\text{tmp}_2\text{AlI} \cdot \text{py}$ in various solvents at ambient temperature, did not lead to substitution of the iodine atom by the weakly coordinating ions BR_4^- , even after a reaction time of several weeks. In the case of the reaction with AgBPh_4 , the only species detectable after heating were tmp_2AlPh (**5a**) and $\text{BPh}_3 \cdot \text{py}$ (**5b**). This implies that $[\text{tmp}_2\text{Al}(\text{py})]\text{BPh}_4$ is formed initially, which then decomposes to give **5a** and **5b**. The aluminum compound **5a** has been synthesized independently from PhLi and tmp_2AlCl ^[17].

Upon reaction with AgOtos ($\text{Otos} = \text{tosylate}$), **4a** gives only the tetracoordinated, covalent product of nucleophilic substitution, $\text{tmp}_2\text{AlOtos} \cdot \text{py}$ (**5c**). Likewise, a mixture of AgBF_4 , 2,6-lutidine (= lut) and **1b** yields the adduct $\text{tmp}_2\text{Al}(\text{BF}_4) \cdot \text{lut}$ (**5d**). Replacing the sterically hindered, less powerful donor 2,6-lutidine by pyridine leads to $\text{tmp}_2\text{Al}(\text{BF}_4) \cdot \text{py}$ (**5e**). The latter compound, molecular in *n*-pentane solution, dissociates in CH_2Cl_2 to give an ion

pair $[\text{tmp}_2\text{Al}(\text{py})]\text{BF}_4$. This dissociation is accompanied by dramatic shifts of the ^{11}B - and ^{19}F -NMR resonances.



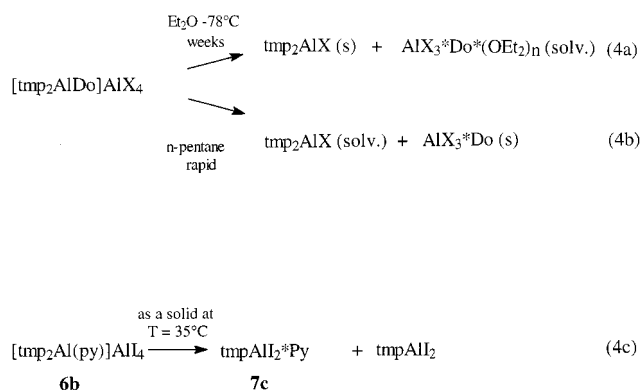
As all the tested tetraphenylborates and tetrafluoroborates turned out to be either unstable (due to dephenylation) or too basic (formation of adducts) to give ionic compounds of the type $[\text{tmp}_2\text{Al}(\text{Do})]\text{Y}$, a different approach was evaluated, in which strong halide acceptors were employed in order to induce a reaction according to Eq. 3a.



	6a	6b	6c	6d	6e	6f
X	Br	I	I	I	I	I
Do	iq	py	γ -pic	4-tBu-Py	iq	acr

Addition of one equivalent of AlX_3 ($\text{X} = \text{Br}, \text{I}$) to solutions of $\text{tmp}_2\text{AlX} \cdot \text{Do}$ ($\text{X} = \text{Br}, \text{I}$) in CH_2Br_2 (for **6a**) or in aromatic solvents such as toluene leads smoothly to the ionic compounds $[\text{tmp}_2\text{Al}(\text{iq})]\text{AlBr}_4$ (**6a**), $[\text{tmp}_2\text{Al}(\text{py})]\text{AlI}_4$ (**6b**), $[\text{tmp}_2\text{Al}(4\text{-Me-py})]\text{AlI}_4$ (**6c**), $[\text{tmp}_2\text{Al}(4\text{-}t\text{Bu-py})]\text{AlI}_4$ (**6d**), $[\text{tmp}_2\text{Al}(\text{iq})]\text{AlI}_4$ (**6e**), and $[\text{tmp}_2\text{Al}(\text{acr})]\text{AlI}_4$ (**6f**), (iq = isoquinoline, acr = acridine). If a solution of $\text{tmp}_2\text{AlCl} \cdot \text{thf}$ (**2a**) in THF is treated with AlCl_3 , only the adduct $\text{AlCl}_3 \cdot (\text{thf})_2$ is formed, according to the ^{27}Al -NMR spectrum. In contrast to the iodide $[\text{tmp}_2\text{Al}(\text{acr})]\text{AlI}_4$ (**6f**), ad-

dition of AlBr_3 to a 1:1 mixture of tmp_2AlBr (**1b**) and acridine leads to exclusive formation of $\text{AlBr}_3 \cdot \text{acr}$ (**7d**), leaving **1b** uncoordinated. The tetraiodoaluminates were found to be the most stable of all the tetrahaloaluminates. Nevertheless, NMR spectroscopic evidence was found even for the formation of ionic tetrachloroaluminates. Solutions of **6b–f** in aromatic hydrocarbons or CH_2Cl_2 are stable for weeks at ambient temperature, but addition of *n*-pentane (in an attempt to induce crystallization) results in slow decomposition to give tmp_2AlI (**1c**) and $\text{AlI}_3 \cdot \text{Do}$. This was proven by the isolation and full characterization of $\text{AlI}_3 \cdot \text{iq}$ (**7a**) and $\text{AlI}_3 \cdot (4\text{-}t\text{Bu-py})$ (**7b**), as well as by NMR spectroscopic characterization of tmp_2AlI (**1c**) (see Eq. 4a and 4b)^[15]. The preparation of **6b** also proceeds smoothly in Et_2O , but storing the concentrated solution at -78°C in the hope of obtaining crystals leads to decomposition into soluble $\text{AlI}_3 \cdot \text{py} \cdot (\text{OEt}_2)_n$ and insoluble tmp_2AlI (**1c**), according to Eq. 4c^[15]. Upon standing for one week at 35°C , solid **6b** disproportionates into tmpAlI_2 and $\text{tmpAlI}_2 \cdot \text{py}$ (**7c**).



Characterization

Compared to the shifts and half-widths of the ^{27}Al -NMR signals of the tricoordinated alanes tmp_2AlX **1a–c** ($\delta^{27}\text{Al} = 130\text{--}131$, $\Delta_{1/2} = 9100\text{--}13700$ Hz)^[15], the signals of the adducts **2–4** are shifted by 30–60 ppm to higher field due to the higher electron-density at the aluminum center and are narrower. As compounds **2–4** have tetracoordinated aluminum atoms, and thus the local symmetry at the aluminum nuclei is increased (as compared to **1a–c**), the average half-widths of the ^{27}Al -NMR signals are reduced to approximately 6800 Hz (see Table 1)^{[18][19]}. Single sets of lines are observed in the ^1H - and ^{13}C -NMR spectra of the tmp ligands, indicating free rotation about the Al–N bond as well as rapid inversion of the piperidiny ring. Compared to the halides **1a–c**, the signals are shifted downfield [by about 0.3 ppm (^1H NMR) and 2.7 ppm (^{13}C NMR)]. Moreover, the chemical shifts show a strong solvent dependence. In CDCl_3 , the signals are found at higher field than in C_6D_6 . The decrease in Lewis acidity in the series $\text{Al–I} > \text{Al–Br} > \text{Al–Cl}$ ^{[3][4]} and the bond enthalpy order Al–X ($\text{Al–I} < \text{Al–Br} < \text{Al–Cl}$)^[6] are mirrored by the chemical shifts of the tmp methyl groups. For $\text{tmp}_2\text{AlCl} \cdot \text{iq}$ (**2b**), the methyl protons give rise to a signal

at $\delta = 1.29$; for $\text{tmp}_2\text{AlBr} \cdot \text{iq}$ (**3c**) at $\delta = 1.37$, and for $\text{tmp}_2\text{AlI} \cdot \text{iq}$ (**4b**) at $\delta = 1.41$. Similarly, the methyl protons resonate at $\delta = 1.58$ in $\text{tmp}_2\text{AlBr} \cdot \text{py}$ (**3b**) and at $\delta = 1.62$ in $\text{tmp}_2\text{AlI} \cdot \text{py}$ (**4a**). These changes point to a predissociation of the weakest Al–X bond (Al–I). The aluminum centre thus becomes more positively charged (see **B**), and the resonances appear at lower field.

Table 1. ^{27}Al chemical shifts and line-widths, and selected ^1H - and ^{13}C -NMR data of compounds **2b**, **3a–c**, and **4a–c**

Compound (sol.v.)	2b [CDCl ₃]	3b [C ₆ D ₆]	3c [CDCl ₃]	3a [C ₆ D ₆]	4a [C ₆ D ₆]	4b [CDCl ₃]	4c [C ₆ D ₆]
$\delta^{27}\text{Al}$ ^[a]	102	96	109	125	92	108	76
$\Delta_{1/2}$ ^[b]	8.300	4.360	7.500	8.000	4.900	8.900	5.900
$\delta^1\text{H}$ ^[a]	10.07	s9.25 s	10.17	s3.76 t	9.06 s	10.21	s9.27 s
	9.11 d ^[e]		9.18 d ^[c]			9.21 d ^[d]	
$\delta^{13}\text{C}$ ^[a]	155.1	150.4	155.7	68.3	148.0	155.3	150.2

^[a] In ppm. – ^[b] In Hz. – ^[c] $^3J(\text{H,H}) = 7.4$ Hz. – ^[d] $^3J(\text{H,H}) = 6.4$ Hz. – ^[e] $^3J(\text{H,H}) = 6.6$ Hz.

The chemical shifts of hydrogen and carbon atoms adjacent to the heteroatoms of the donor molecules proved to be valuable indicators in ascertaining whether or not a compound $\text{tmp}_2\text{Al}(\text{Do})\text{Y}$ (Y = anion or ligand) is dissociated into an ion pair (see Table 2). In comparison with the free pyridine bases, the resonances for these bases in the adducts **2–4** are shifted downfield by 0.6 to 1 ppm (^1H -NMR) and by 0.6 to 3.5 ppm (^{13}C -NMR), respectively.

The decomposition products of the tetraphenylborate, as described by Eq. 2b, were identified by their ^1H -, ^{13}C -, and ^{27}Al -NMR shifts, as reported in the literature (tmp_2AlPh , **5a**)^[17], or by the known ^{11}B -NMR shift of $\delta = 5.0$ ^[20]. Further evidence was provided by the ^1H -NMR spectrum, elemental analysis, and X-ray crystal structure determination of $\text{BPh}_3 \cdot \text{py}$ (**5b**)^[21].

Since $\text{tmp}_2\text{AlOtos} \cdot \text{py}$ (**5c**) exhibits a ^{27}Al -NMR signal in the same range as the adducts **2–4** ($\delta^{27}\text{Al} = 97$, $\Delta_{1/2} = 5500$ Hz), as well as a similar shift of the *ortho*-protons on the pyridine ring ($\delta^1\text{H} = 9.29$, cf. the data in Table 1), it appears that this species is not ionic. A very similar situation is found for $\text{tmp}_2\text{Al}(\text{lut})\text{BF}_4$ (**5d**). In its ^{27}Al -NMR spectrum, a line at $\delta = 1$ ($\Delta_{1/2} = 3400$ Hz) is found, too narrow to be attributable to a tricoordinated aluminum centre. Moreover, the ^{11}B -NMR spectrum consists of a single, broadened line at $\delta^{11}\text{B} = 17.9$. Due to the coordination at the aluminum centre, the resonance is deshielded by 18 ppm compared to the free, ionic tetrafluoroborate^[20]. Similarly, a solution of $\text{tmp}_2\text{Al}(\text{py})\text{BF}_4$ (**5e**) in pentane exhibits a signal at $\delta^{11}\text{B} = 19.3$. If the spectrum is recorded in CDCl_3 or CH_2Cl_2 , a line at $\delta^{11}\text{B} = 0.9$ is observed, indicating the presence of uncoordinated, free BF_4^- ^[20]. This is accompanied by correspondingly dramatic differences in the ^{19}F -NMR signals. Whereas in pentane a broadened resonance at $\delta^{19}\text{F} = -111$ (analogous to **5d**: $\delta^{19}\text{F} = -104.5$ and -111.0) is found, in CDCl_3 a 1:1:1:1 quartet at $\delta^{19}\text{F} = -151$ with $^1J(\text{B,F}) = 12$ Hz supports the salt formation [cf. F_3BOH , $^1J(\text{B,F}) = 16.4$ Hz; $\text{F}_3\text{B} \cdot \text{N}(\text{H})_x\text{Me}_{3-x}$, $x = 0\text{--}3$,

$^1J(\text{B},\text{F}) = 15.1$ to 16.4 Hz]^[20]. The ^{27}Al -NMR signal of **5e** in CH_2Cl_2 is additional evidence for the ionic behavior in polar solvents: a very broad signal is observed, covering the full spread of the spectrum. The ^1H -NMR signals of the *ortho*-protons on the pyridine ring also reflect this change: the shift for **5e** ($\delta = 8.71$) is consistent with an ionic structure {cf. $[\text{tmp}_2\text{Al}(\text{py})]\text{AlI}_4$, (**6b**), $\delta^1\text{H} = 8.59$ }, but not with the adduct $\text{tmp}_2\text{AlI} \cdot \text{py}$ (**4a**), where the corresponding signal appears at $\delta = 9.06$.

Compared to the adducts **2–4**, the formation of the ionic species **6a–f** is accompanied by dramatic changes in the line-widths of the ^{27}Al -NMR signals. Whereas **2–4** exhibit average line widths of 6800 Hz, a single sharp line attributable to the AlX_4^- fragment ($\Delta_{1/2} = 17$ to 134 Hz) is found for compounds **6a–f**. The second aluminum nucleus, assumed to be tricoordinated, should contribute to the spectra with a very broad line. Due to the presence of highly symmetrical, NMR-sensitive and unsymmetrical, tricoordinated aluminum centres, this line is not usually detected {e.g. in the ambient temperature ^{27}Al -NMR spectrum of $[\text{Al}(\text{O}i\text{Pr})_3]_4$ one sharp line, assigned to the central, hexacoordinated aluminum atom is readily detected ($\delta^{27}\text{Al} = -2.62$, $\Delta_{1/2} = 102$ Hz), while signals due to the tetraordinated aluminum atoms are not seen^{[19]}}. As the chemical shifts of the tetrahaloaluminates (**6a**: $\delta^{27}\text{Al} = 104$; **6b–e**: $\delta^{27}\text{Al} = 50$ – 55 ; **6f**: $\delta^{27}\text{Al} = -22$) are, with the exception of **6f**, found at lower field than those reported in the literature $[\text{AlBr}_4^-$: $\delta^{27}\text{Al} = 80$ – 83 , AlI_4^- : $\delta^{27}\text{Al} = -27$ (CH_2Cl_2)]^[19], a weak coordination of the anions to the cationic aluminum center is indicated. Considering the narrow line-width for **6a–f** ($\Delta_{1/2} = 17$ – 134 Hz), this interaction cannot be very strong, since the aluminum nucleus is very sensitive to a disturbance of symmetry. Due to the positive charge of **6a–f**, the ^1H - and ^{13}C -NMR signals of the protons and the carbon atoms adjacent to the heteroatoms of the donor molecules are shifted by about 0.4 ppm (^1H NMR) and 1–3 ppm (^{13}C NMR), respectively, to higher field, compared to the corresponding signals in compounds **2–4**. This is a characteristic feature for these ionic com-

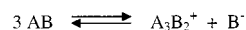
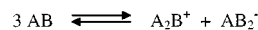
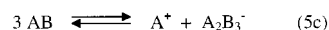
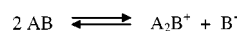
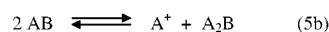
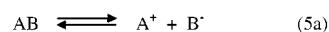
As the calculated Al–N bond lengths and N–Al–N bond angles are very similar (to within ± 0.01 Å and $\pm 1^\circ$), similar NMR spectroscopic data can be expected.

Addition of *n*-pentane to a solution of **6b** or **6d** in aromatic hydrocarbons leads to disproportionation according to Eq. 4c. In solution, the characteristic chemical shifts of tmp_2AlI (**1c**) could be detected (^1H -, ^{13}C -, ^{27}Al -NMR)^[15]. Crystals of $\text{AlI}_3 \cdot 4\text{-}t\text{Bu-py}$ (**7b**), which separated on cooling to 5°C , were characterized spectroscopically and analytically, as was a sample of $\text{AlBr}_3 \cdot \text{acr}$ (**7d**), obtained according to Eq. 3b. Due to the highly symmetrical coordination at the aluminum nuclei, these compounds give sharp lines at $\delta^{27}\text{Al} = 51$ ($\Delta_{1/2} = 46$ Hz) (**7b**) and $\delta = 83$ ($\Delta_{1/2} = 34$ Hz) (**7d**). Since only one distinct line was observed in each ^{27}Al -NMR spectrum, dissociation into ionic species as found for $\text{AlCl}_3 \cdot \text{py}_2$ can be ruled out^[5]. Moreover, $\text{AlI}_3 \cdot \text{iq}$ (**7a**) precipitated under these conditions as a molecular adduct. It was only characterized by its X-ray crystal structure.

In the solid state, **6b** decomposes into tmpAlI_2 and $\text{tmpAlI}_2 \cdot \text{py}$ (**7c**) (Eq. 4c). This is demonstrated by its ^{27}Al -NMR spectrum: one signal at $\delta^{27}\text{Al} = 69$ ($\Delta_{1/2} = 2640$ Hz) is observed for **7c**, the half-width of which resembles that of signals of other $\text{tmpAlX}_2 \cdot \text{Do}$ compounds^{[15][19]}. The ^1H - and ^{13}C -NMR shifts of **7c** are very similar to those observed for $\text{tmp}_2\text{AlI} \cdot \text{py}$ (**4a**), differing by only about 0.01 ppm ($\delta^1\text{H}$) and 0.1 ppm ($\delta^{13}\text{C}$). Thus, it is most likely that **7c** is present in solution as a tetraordinated adduct.

Conductivity Measurements

To prove the formation of ions, conductivity measurements were carried out on well-defined CH_2Cl_2 solutions of **5d**, **6a–b**, **e** and the dissociation patterns were deduced from the calculated gradients of the resulting Fuoss-Kraus plots^[22]. These salts are stable in CH_2Cl_2 solution and do not undergo halogen-exchange with the solvent, as is observed for AlX_3 solutions ($\text{X} = \text{Br}, \text{I}$). The gradient of these plots gives an indication of the ion pair formation from the undissociated parent species. An equilibrium as described by Eq. 5a corresponds to a gradient of -0.5 , that according to Eq. 5b exhibits a gradient of 0, while a dissociation pattern described by Eq. 5c is represented by a value of 0.5.



A solution of **5d** in CH_2Cl_2 shows no electrical conductivity and thus this compound remains as a molecular adduct, as already shown by its NMR data. Solutions of **6a**, **b**, **e** exhibit electrical conductivity, indicating ion pair formation. The gradient of the plot for **6b** reaches a value of approximately -0.6 , indicating a reaction according to Eq. 5a. However, the gradients for **6a**, **e** are -0.1 and -0.2 ,

Table 2. Selected NMR data of compounds **6**

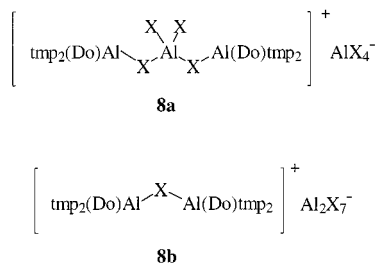
Compound	$\delta^{27}\text{Al}$ [ppm]	$\Delta_{1/2}$ [Hz]	$\delta^1\text{H}$ [ppm]	$\delta^{13}\text{C}$ [ppm]
6a [CDCl_3]	104	66	9.89 s ^[a] , 8.94 d ^[b]	152.5
6b [C_6D_6]	50	134	8.59 s ^[a]	147.0
6c [C_6D_6]	51	35	8.47 s ^[a]	146.9
6d [C_6D_6]	51	75	8.54 s ^[a]	146.6
6e [CDCl_3]	55	17	9.70 s ^[a] , 8.75 d ^[b]	152.4
6f [CDCl_3]	-22.0	70	8.80 s ^{[a][c]} , 8.21 d ^[d]	148.7

[a] Broad. – [b] $^3J(\text{H},\text{H}) = 6.4$ Hz. – [c] At C7, *trans* to N1. – [d] $^3J(\text{H},\text{H}) = 8.1$ Hz.

pounds (see Table 2 and compare with the data in Table 1).

Single sets of lines are observed for the tmp ligand in **6**, indicating free rotation about the Al–N bond and rapid inversion of the piperidiny ring. Compared to the adducts **2–4**, the signals appear at higher field and resemble those found for the halides **1b–c**. This is in line with calculated AM1 data^[29] for **1b**, **c** and $[\text{tmp}_2\text{Al}(\text{py})]\text{AlX}_4$ ($\text{X} = \text{Br}, \text{I}$).

respectively. This corresponds with ion formation according to Eq. 5a and Eq. 5b, with a greater percentage of the dissociation behavior conforming to Eq. 5b. **8a** and **8b** represent two possible structures of the ionic products formed according to Eq. 5b.



Crystal Structures

The adducts of tmp_2AlCl (**2a**, **b**) and tmp_2AlBr (**3a**) crystallize in the monoclinic space group $P2_1/n$ with four molecules in the unit cell, while $\text{tmp}_2\text{AlBr} \cdot \text{py}$ (**3b**) and $\text{tmp}_2\text{AlI} \cdot \text{py}$ (**4a**) are isotypical having the monoclinic space group $C2/c$ ($Z = 8$). Structural parameters of these compounds are given in Table 3, crystallographic details in Table 6.

Table 3. Selected bonding parameters of compounds **2a**, **b**, **3a**, **b**, and **4a**

Compound	2a	2b	3a	3b	4a
Bond lengths [Å]					
d(Al–X)	2.227(3)	2.220(1)	2.408(2)	2.429(2)	2.704(1)
d(Al–N1)	1.836(5)	1.844(2)	1.836(4)	1.838(4)	1.849(3)
d(Al–N2)	1.843(6)	1.851(3)	1.844(4)	1.844(4)	1.854(4)
d(Al–N3/O1)	2.041(7)	1.913(2)	1.928(4)	2.030(4)	2.022(3)
Bond angles [°]					
N1–Al–N2	126.0(3)	126.6(1)	126.7(2)	125.7(2)	126.1(2)
N1–Al–X	106.3(2)	104.22(8)	104.9(2)	105.2(1)	104.4(1)
N2–Al–X	113.8(2)	115.40(8)	115.2(2)	115.5(1)	116.0(1)
N3/O1–Al–X	95.7(2)	95.13(7)	94.3(2)	93.6(1)	92.7(1)
N3/O1–Al–N1	111.6(3)	111.8(1)	111.9(2)	111.7(2)	111.9(2)
N3/O1–Al–N2	99.1(3)	99.2(1)	98.9(2)	100.4(2)	100.7(2)
Al–N1–C1	127.4(4)	127.4(2)	125.9(4)	127.5(3)	127.4(3)
Al–N1–C5	116.8(4)	117.0(2)	116.7(3)	114.9(4)	116.8(3)
Al–N2–C10	124.7(4)	123.9(2)	124.8(3)	125.8(3)	124.9(2)
Al–N2–C14	121.9(4)	121.5(2)	121.2(4)	120.8(3)	121.0(2)
Sum of bond angles [°]	359.5	359.8	358.8	358.8	359.4
$\Sigma(\text{N1})$	359.5	359.8	359.7	359.6	359.6
$\Sigma(\text{N2})$	360.0	360.0	359.6	359.9	360.0
Torsion angles [°]					
C1–N1–Al–X	69.81	75.95	75.06	72.36	—
C5–N1–Al–X	57.20	60.41	60.49	59.88	—
C10–N2–Al–X	29.23	35.06	22.49	26.69	—
C14–N2–Al–X	19.68	19.39	16.27	18.36	—

Each of the aluminum centres in the five compounds is coordinated in a distorted tetrahedral fashion by one tmp ligand in the chair conformation, one tmp ligand in the twist conformation, the N or O atom of the donor molecule, and the halogen atom. The N and O atoms of the ligands are tricoordinated and exhibit bond angle sums close to 360° (358.8 – 360.0°). The most interesting feature of these adducts are the long Al–X bond lengths: 2.220(1) to 2.227(3) Å for X = Cl; 2.408(2) to 2.429(2) Å for X =

Figure 1. Molecular structure of **2a** in the solid state. Thermal ellipsoids are shown at a 25% probability level

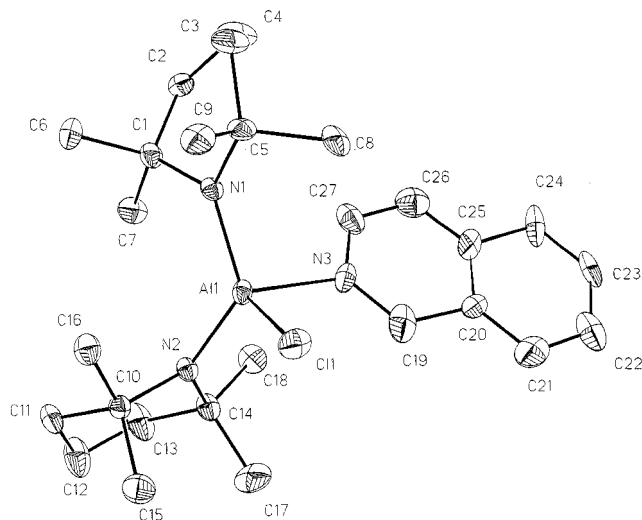


Figure 2. Molecular structure of **2b** in the solid state. Thermal ellipsoids are shown at a 25% probability level

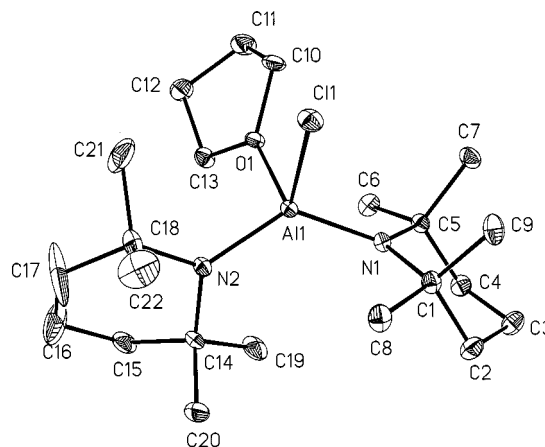


Figure 3. Molecular structure of **3a** in the solid state. Thermal ellipsoids are shown at a 25% probability level

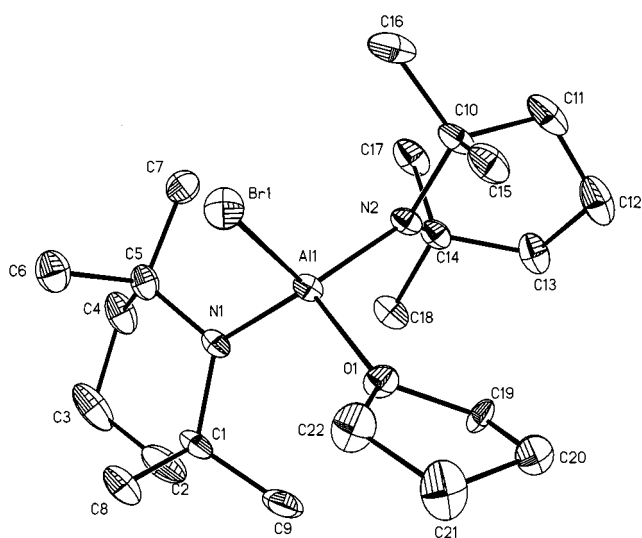


Figure 4. Molecular structure of **3b** in the solid state. Thermal ellipsoids are shown at a 25% probability level

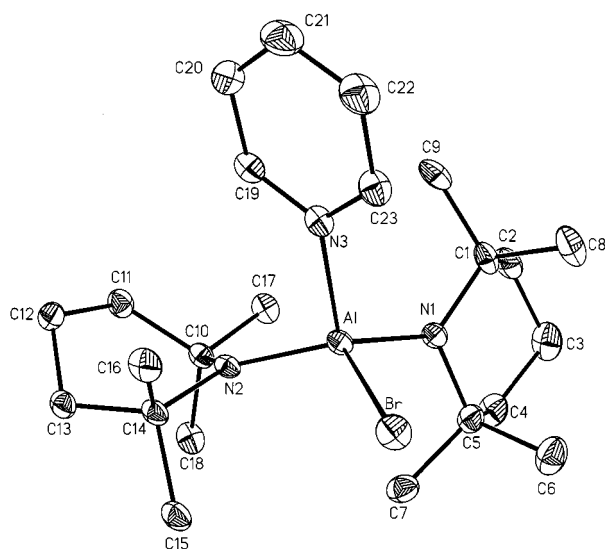
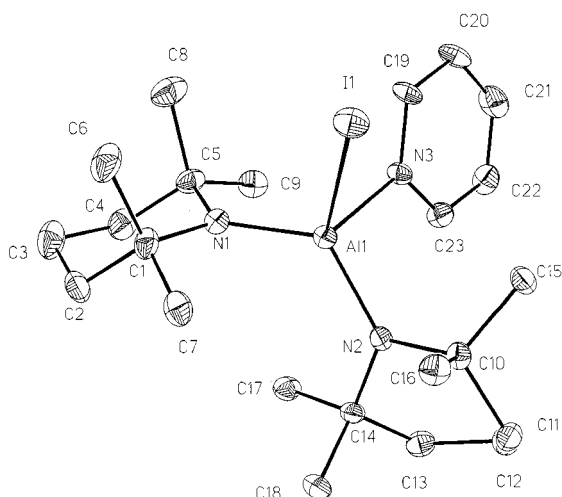


Figure 5. Molecular structure of **4a** in the solid state. Thermal ellipsoids are shown at a 25% probability level



Br, and 2.704(1) Å for X = I. The Al–N bond lengths fall in a narrow range, varying only from 1.836(5) to 1.854(4) Å. There are no differences in the bond distances between the tmp ligand present in the chair conformation and that in the twist conformation. Al–Do distances range from 1.913(2) to 1.928(4) Å (THF) and from 2.022(3) to 2.041(7) Å (pyridine bases). As the tmp ligands are quite bulky, the N–Al–N bond angle [125.7(2) to 126.7(2)°] shows a considerable deviation from the tetrahedral bond angle of 109.5°.

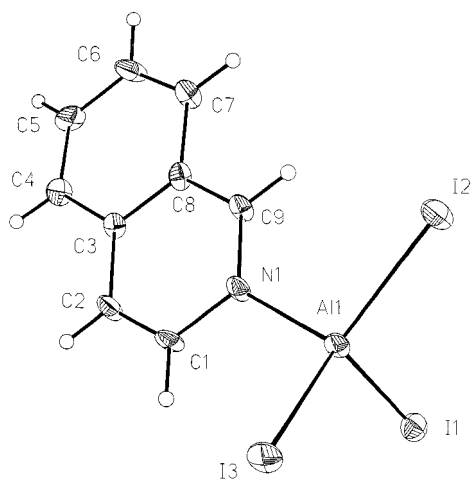
Compared to the sums of their covalent radii (Al–Cl 2.10, Al–Br 2.28, Al–I 2.48 Å, corrected for ionic contributions by the Schomaker-Stevenson method^[23]), which normally correspond well with the experimental Al–X atom distances (X = Cl, Br, I), the bond lengths found for tmp₂AlX·Do (**2–4**) are unusually long. They exceed the sums of their covalent radii by 12 (Cl) to 23 pm (I). The

bond lengths $d(\text{Al}–\text{Cl})$ in **2a**, **b** and the Al–Cl distance found in the molecular adduct Me₂AlCl·NH₂*t*Bu [2.204(2) Å]^[10] reveal that the adducts **2a**, **b** are in a state of predissociation {cf. the related salts [Me₂Al(NH₂*t*Bu)₂]X, X = Br, I}^[10]. Thus, Al–Cl bond lengths shorter than those in the adducts **2a**, **b** have been observed even for usually longer bridging Al–Cl–Al distances, e.g. in the centrosymmetric organoaluminum dichloride Ar(Cl)Al(μ-Cl)₂Al(Cl)Ar (Ar = 2,6-Me₂C₆H₃), where the Al–Cl bond lengths amount to 2.195(2) Å, terminal: 2.125(2) Å]^[24]. This is also true for **3–4**, which exhibit long Al–X distances in the range typical of bridging Al–X–Al units, e.g. of the same order as those in (*t*Bu₂Alμ-X)₂ [X = Br 2.463(3) Å, X = I 2.708 Å]^[25] or in (trip₂Alμ-Br)₂ [$d(\text{Al}–\text{Br})$ = 2.475(4) and 2.500(3) Å; trip = 2,4,6-*i*Pr₃C₆H₂]^[26]. This elongation can be viewed as the initial stage of dissociation. For the Al–I bond in particular, a strongly polar Al^{δ+}–I^{δ–} bonding situation follows [cf. Me₂AlI·NMe₃; $d(\text{Al}–\text{I})$ = 2.58 Å]^[28], which also explains the poor solubility of these compounds in non-polar solvents.

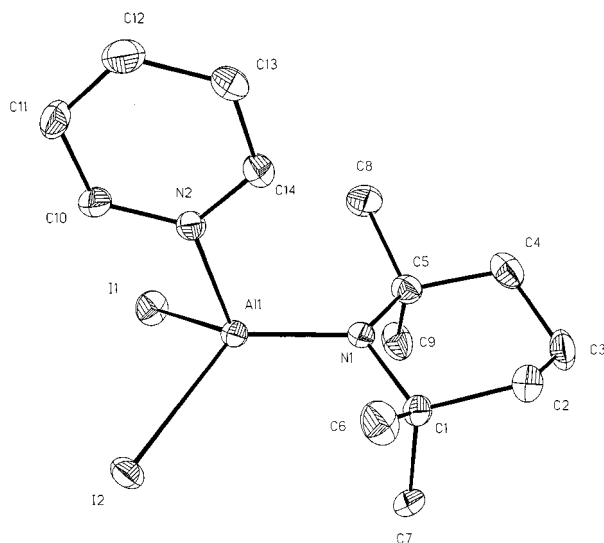
Crystals of the adduct AlI₃·iq (**7a**) are monoclinic, space group *C2/c* (*Z* = 8, Figure 7). For compound tmpAlI₂·py (**7c**), the monoclinic space group *P2₁/n* with four molecules in the unit cell has been determined (Figure 8). The aluminum atoms in these adducts are tetracoordinated by the pyridine base, the iodine atoms, and the tmp ligand. The latter substituent adopts the chair conformation and possesses a planarized nitrogen centre (sum of bond angles 356.2°). The Al–N distance to the donor molecule decreases from 1.978(5) Å (**7c**) to 1.947(9) Å (**7a**) (cf. the adducts **2–4** in Table 2) as the number of iodine atoms increases. This gives an indication that AlI₃ is a stronger Lewis acid than tmpAlI₂. For AlCl₃·NMe₃, $d(\text{Al}–\text{N})$ amounts to 1.96 Å^[4], while for *cyclo*-Me₂NCH₂CH₂(Et)–NAlCl₂, this distance is 1.963(2) Å^[27]. However, in **7c**, the Al–N bond to the tmp ligand is short [1.809(5) Å] and resembles that in [tmp(Br)Alμ-OEt]₂, [$d(\text{Al}–\text{N})$ = 1.810(3) Å]^[15]. Thus, the difference between the coordinative Al–N linkage and the covalent Al–N bond is about 0.17 Å. Given these bonding parameters for **7a**, **c**, it is not surprising that the Al–I bond lengths in **7a** are – on average – 6.5 pm shorter than those in **7c** [**7a**: 2.500(4) to 2.510(4), **7c**: 2.572(2) and 2.573(2) Å]. This is in accord with a decrease of the Lewis acidity of the aluminum centre in **7c** and compares well with the $d(\text{Al}–\text{I})$ of 2.58 Å observed in Me₂AlI·NMe₃^[28].

Semiempirical and Ab Initio Calculations

Semiempirical AM1^[29] calculations have been performed in order to investigate the extent of steric shielding and the bond strength factors that are necessary to favor ionization. Thus, the structures of the cations [(R₂N)₂Al(py)]⁺ and the salts [(R₂N)₂Al(py)]⁺AlCl₄[–], as well as of the halide-bridged adduct compounds (R₂N)₂(py)Al–Cl–AlCl₃ were computed (R = Me, Et, *i*Pr, and R₂N = tmp). The heats of formation of the respective minimum geometries and the shortest Al–ClAlCl₃ distances are presented in Table 4.

Figure 6. Molecular structure of **7b** in the solid state. Thermal ellipsoids are shown at a 25% probability level^[a]

^[a] Selected atom distances [Å] and bond angles [°]: Al1–I1 2.500(4), Al1–I2 2.508(4), Al1–I3 2.510(4), Al1–N1 1.947(9); N1–Al1–I1 104.8(3), N1–Al1–I2 106.7(3), N1–Al1–I3 106.8(3), I1–Al1–I2 112.2(1), I1–Al1–I3 112.2(2), I2–Al1–I3 113.5(1).

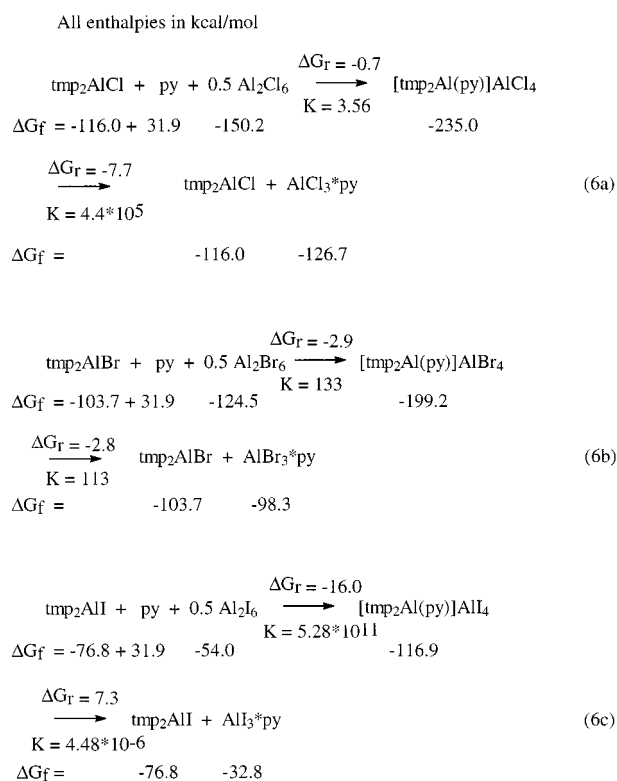
Figure 7. Molecular structure of **7c** in the solid state. Thermal ellipsoids are shown at a 25% probability level^[a]

^[a] Selected atom distances [Å] and bond angles [°]: Al1–I1 2.573(2), Al1–I2 2.572(2), Al1–N1 1.809(5), Al1–N2 1.978(5); N1–Al1–I1 122.3(2), N1–Al1–I2 123.5(2), N1–Al1–N2 106.3(2), I1–Al1–N2 103.4(2), I2–Al1–N2 101.2(2), I1–Al1–I2 96.89(6), C1–N1–Al1 120.1(4), C5–N1–Al1 118.7(4), C1–N1–C5 117.4(5).

Table 4. AM1 calculated heats of formation of various model compounds

R ₂ N	Heat of formation [(R ₂ N) ₂ Al(py)] ⁺	Heat of formation (R ₂ N) ₂ (py)Al ⁺ –Cl –AlCl ₃	Al ⁺ –ClAlCl ₃ ⁺ <i>d</i> (Al–Cl) [Å]
Me ₂ N	+113.1 kcal/mol	–231.1 kcal/mol	2.42
Et ₂ N	+93.3 kcal/mol	–251.7 kcal/mol	2.41
<i>i</i> Pr ₂ N	+82.5 kcal/mol	–254.3 kcal/mol	2.42
tmp	+90.1 kcal/mol	–235.0 kcal/mol	4.45

The free cations exhibit positive heats of formation (in the range +82.5 to +113.1 kcal/mol), whereas the tetrachloroaluminum compounds are exergonic by –231.1 to –254.3 kcal/mol. Shielding of the aluminum center by the amido ligands R₂N (R = Me, Et, *i*Pr) is insufficient to prevent coordination of one chlorine atom [*d*(Al–Cl)] of the tetrachloroaluminate to the aluminum center of the cation: 2.41–2.42 Å. It is only the sterically most demanding amido ligand, tmp, that allows the induction of ionization, as demonstrated by the shortest Al–Cl distance of 4.45 Å. In another series of calculations, the enthalpies for the formation of [tmp₂Al(py)]AlX₄ (X = Cl, Br, I), as well as for the observed decomposition reactions of the salts into tmp₂AlX and AlX₃·py, were calculated from the computed heats of formation of every compound involved (see Scheme 1) using Hess' rule.

Scheme 1. AM1 computed heats of formation and enthalpies of reaction for the formation and decomposition of [tmp₂Al(py)]AlX₄ (X = Cl, Br, I)

Two opposing trends are observed: whereas the heat of formation for the salt [tmp₂Al(py)]AlX₄ decreases on going from the chloride to the iodide (but still remains exergonic), the enthalpies for the formation of the salts increase in this direction. In fact, in the case of the iodide, the salt is stable with respect to decomposition into tmp₂AlI and AlI₃·py. This is partly due to the thermodynamically less favored Al–I bond [*E*(Al–Cl) = 494 kJ/mol; *E*(Al–I) = 364 kJ/mol]^[6], but is mainly attributable to the contribution of electrostatic stabilization of the tetraiodoaluminate, since the decomposition products, which also contain Al–X bonds, are less favored on going from the chloride to the iodide.

As no X-ray crystal structures of the ionic species could be determined, an *ab initio* study (MP2/6-31+G*)^[30] of two model compounds $[(\text{H}_2\text{N})_2\text{Al}(\text{Do})]^+$ (Do = NH_3 **8a**, py **8b**) was performed, in order to assess the structural parameters of these cations. The minimum structures of the cations **8a**, **b** are depicted in Figure 9, and their structural parameters are given in Table 5.

Figure 8. Computed structures of $[(\text{H}_2\text{N})_2\text{Al}(\text{NH}_3)]^+$ (**8a**) and $[(\text{H}_2\text{N})_2\text{Al}(\text{py})]^+$ (**8b**)

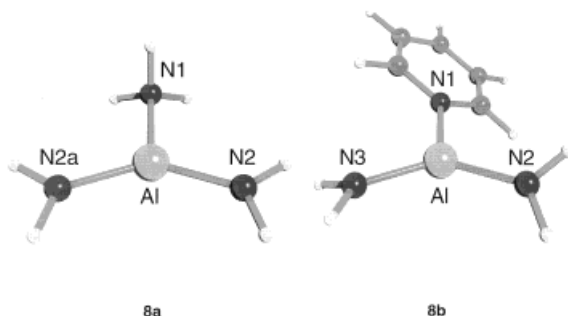


Table 5. Selected *ab initio* calculated bonding parameters for the two model cations, **8a**, **b**

Compound ^[a]	Sym.	$d(\text{Al}-\text{N})$ [Å]	$d(\text{Al}-\text{L})$ [Å]	N-Al-N [°]	$q(\text{Al})$ [e]	$q(\text{N})$ [e]	$q(\text{L})$ [e]	B.O. Al-N	LP* ^[b] (Al)
$[(\text{H}_2\text{N})_2\text{Al}(\text{NH}_3)]^+$ 8a	Cs	1.758	1.996	139.34	2.12	-1.54	-1.26	0.62	0.19
$[(\text{H}_2\text{N})_2\text{Al}(\text{py})]^+$ 8b	Cl	1.764	1.947	136.86	2.14	-1.54	-0.78	0.60	0.13

^[a] All calculations MP2/6-31+G*. – ^[b] Number of electrons in $3p_z$ orbital of Al.

The tricoordinated aluminum cations **8a**, **b** represent highly charged species [$q(\text{Al}) = +2.12\text{e}$ and $+2.14\text{e}$, $q(\text{N}) = -1.54\text{e}$ and -1.54e , $q(\text{Do}-\text{N}) = -1.26\text{e}$ and -0.78e], with short Al–N bond lengths of 1.758 Å (**8a**) and 1.764 Å (**8b**) as well as wide N–Al–N bond angles of 139.3° and 136.8°, respectively. The Al–N distances to the nitrogen atoms of the donor molecules reflect their degree of hybridization. As expected, for the sp^3 -hybridized donor NH_3 , a longer Al–N bond length (1.996 Å) was calculated, compared to that for the aromatic pyridine donor [$d(\text{Al}-\text{N}) = 1.947$ Å]. According to NBO analysis, the $3p_z(\text{Al})$ orbital is populated with 0.19 (**8a**) and 0.13 (**8b**) electrons, indicating the presence of only weak $\text{pp}(\pi)$ Al–N bonding. This compares well with the calculated minimum structures of $(\text{H}_2\text{N})_2\text{AlY}$ [$\text{Y} = \text{Cl}, \text{OH}, \text{SH}, \text{NH}_2, \text{PH}_2, \text{CH}_3, \text{SiH}_3, \text{Al}(\text{NH}_2)_2$]^[17]. For these compounds, it was shown that the Al–N bond is highly polar and that the shorter the Al–N distance, the wider the N–Al–N bond angle^[17]. Since the Al–N bond lengths in **8a**, **b** are 2 pm shorter than in $(\text{H}_2\text{N})_2\text{AlCl}$ (**9**) [the compound with the shortest Al–N bond in the $(\text{H}_2\text{N})_2\text{AlY}$ series, $d(\text{Al}-\text{N}) = 1.782$ Å], the N–Al–N bond angles in **8a**, **b** of 139.3° and 136.8° are widened by about 16° compared to that in the chloride **9** (123.2°). The short Al–N bonds are mirrored by an increased positive charge of 0.16e and 0.18e residing on the aluminum centres of **8a**, **b**, compared to that calculated for the chloride **9**. Since the charge on the nitrogen atoms in **8a**, **b**, and **9** remains almost constant (–1.53 to –1.55e), a strongly polar

Al–N bond is responsible for the short Al–N distances in **8a**, **b**.

Discussion

The aim of this study was the synthesis and characterization of low coordinated, cationic aluminum compounds. In contrast to the $\text{R}_2\text{AlX}/t\text{BuNH}_2$ system described by Atwood et al.^[10], the compounds tmp_2AlX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) could not be forced to ionize by the addition of an excess of a donor molecule. The steric demand of the tmp and donor ligands prevents the formation of cations of the type $\text{tmp}_2\text{Al}(\text{Do})_2^+$ and of adducts of the type $\text{tmp}_2\text{AlX} \cdot \text{Do}_2$. However, comparison of the Al–X bond lengths determined for **2–4**, having conventional terminal and bridging Al–X bonds, reveals that $\text{tmp}_2\text{AlX} \cdot \text{Do}$ shows the early stages of dissociation into $[\text{tmp}_2\text{Al}(\text{Do})]^+\text{X}^-$. Dissociation of compounds of the type $\text{tmp}_2\text{AlX} \cdot \text{Do}$ should be facilitated by weakly coordinating anions X^- . However, such a strategy did not succeed with $\text{X} = \text{BPh}_4^-$, $\text{B}(\text{C}_6\text{F}_5)_4^-$, BF_4^- , or tosylate. Instead, decomposition reactions or coordination of the various anions occurred. Nevertheless, the

tetrabromo- and tetraiodoaluminates turned out to be sufficiently non-basic (and suitably large) to stabilize the salts $[\text{tmp}_2\text{Al}(\text{Do})]\text{AlX}_4$ (**6a–f**) in solution. The formation of the AlX_4^- units ($\text{X} = \text{Br}, \text{I}$) is favoured due to the decreasing strength of the Al–X bonds in $\text{tmp}_2\text{AlX} \cdot \text{Do}$ on proceeding from chlorine to iodine, so that the additional stabilization energy provided by ion pair formation governs the overall enthalpy for the decomposition of $[\text{tmp}_2\text{Al}(\text{py})]\text{AlI}_4$ (as predicted by AM1 calculation). Since decomposition products of even tetraiodoaluminates have been found [e.g. $\text{AlI}_3 \cdot \text{iq}$ (**7a**), $\text{AlI}_3 \cdot 4\text{-}t\text{Bu-py}$ (**7b**)], this seems to be contradictory. However, the calculations can only simulate gaseous species in vacuo. As the variations in the reaction enthalpies are small, solvent effects must play a role in the behavior of the tetrahaloaluminate salts. Nevertheless, both the experimental and theoretical approaches indicate that the iodo compounds represent the most stable species. Non-polar solvents disfavor the formation of ionic species of type $[\text{tmp}_2\text{Al}(\text{Do})]\text{AlX}_4$ (**6a–f**), whereas polar donor solvents stabilize the ions, but may also abstract AlX_3 as $\text{AlX}_3 \cdot \text{Do} \cdot (\text{Solv.})_n$ ($n = 1, 2$), providing an alternative decomposition pathway for the system.

Conclusion

The aluminum atoms in the tricoordinated bis(tetramethylpiperidino)aluminum halides **1a–c** are Lewis acidic and form monoadducts of the type $\text{tmp}_2\text{AlX} \cdot \text{Do}$ (**2–4**) with THF and pyridine bases. Since the Al–X ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)

bonds in **2–4** are considerably longer than those in **1a–c**, a tendency towards dissociation into $\text{tmp}_2(\text{Do})\text{Al}^+$ and X^- is indicated. Attempts to prepare salts of the type $[\text{tmp}_2\text{Al}(\text{Do})]\text{Y}^-$ [$\text{Y} = \text{BPh}_4$, $\text{B}(\text{C}_6\text{F}_5)_4$, Otos] led either to decomposition or to the formation of molecular adducts. The solution behavior of $\text{tmp}_2\text{Al}(\text{py})\text{BF}_4$ (**5e**) shows a solvent dependence: in pentane, a tetracoordinated molecular product is observed, while in CH_2Cl_2 or CDCl_3 solution, it dissociates into an ion pair. However, halide abstraction from $\text{tmp}_2\text{AlX} \cdot \text{Do}$ can be achieved by the addition of AlX_3 to generate salts of the type $[\text{tmp}_2\text{Al}(\text{Do})]\text{AlX}_4$, as demonstrated by electrical conductivity in CH_2Cl_2 solution. These experimental results are supported by semiempirical AM1 calculations on the $[(\text{R}_2\text{N})_2\text{Al}(\text{py})]\text{AlX}_4$ species. The results show that the steric demand of the tmp ligand is essential for ion pair formation. The formation of tetraiodoaluminate compounds is favored over that of the corresponding tetrabromo- or tetrachloroaluminates. Further ab initio studies of some model systems explain the presence of short Al–N distances in terms of ionic contributions to the Al–N bond. Whether the Lewis acidic aluminum centre in these cations can act as catalyst, e.g. in olefin polymerization, needs to be evaluated experimentally. Since these salts are highly Lewis acidic, are soluble in aromatic hydrocarbons, and are sterically encumbered so as to possibly induce regioselectivity, these aspects will be investigated and communicated in forthcoming reports.

Once again, the tmp ligand is found to produce a remarkable stabilizing effect and allows the generation of unusual bonding situations, such as the tricoordinated aluminum cations. As yet, the most weakly coordinating anions $\text{CB}_{11}\text{H}_{11}\text{X}^-$ ($\text{X} = \text{H}, \text{Cl}$) have not been tested^[31], but they are certainly good candidates for achieving the formation of $\text{tmp}_2\text{Al}(\text{Do})^+$ cations, or the even more demanding goal of generating the dicoordinated cation tmp_2Al^+ .

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Experimental Section

All manipulations were performed using Schlenk techniques under a dinitrogen or argon atmosphere. All solvents were rigorously dried prior to use and stored under N_2 or argon. Discrepancies in the elemental analyses of a number of compounds can be attributed to insufficient protection against oxidation and hydrolysis of the air- and moisture-sensitive compounds during the weighing procedures. – NMR: Bruker ACP 200, Jeol GSX400 and Jeol GSX270. – IR: Nicolet FT-IR spectrometer model 6000, CsI plates, Nujol. – MS: Varian Atlas CH7 spectrometer.

General Procedure for the Synthesis of the Adducts $\text{tmp}_2\text{AlX} \cdot \text{Do}$ **2–4:** The concentrations of stock solutions of tmp_2AlX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), **1a–c**, in *n*-hexane were determined by titration of aluminum and halide. At ambient temperature, the stoichiometric amount of the appropriate donor was added as a hexane solution. Most of the adducts precipitated immediately. After filtration and concen-

tration of the filtrate to one-third of its original volume, storage at -20°C overnight led to the deposition of well-shaped crystals of **2–4**. Precipitates were washed twice with pentane and dried in vacuo. Yields varied between 80 and 95%. Where suitable crystals for X-ray diffraction studies were required, aromatic solvents or *n*-hexane/THF mixtures proved to be appropriate media for recrystallization.

$\text{tmp}_2\text{AlCl} \cdot \text{iq}$ (2a**):** tmp_2AlCl (43.2 ml, 0.11 M, 4.8 mmol); isoquinoline (0.99 g, 4.8 mmol), yield of **2a**: 1.95 g (86%), m.p. $148–151^\circ\text{C}$. – ^1H NMR (CDCl_3) (400 MHz): $\delta = 1.37$ (t, 8 H, $\text{tmp-}\beta\text{-CH}_2$), 1.29 [s, 24 H, $\text{tmp-C}(\text{CH}_3)_2$], 1.62 (m, 4 H, $\text{tmp-}\gamma\text{-CH}_2$), 7.80 (t, 1 H, iq-CH), 7.93 (m, 3 H, iq-CH), 8.15 (d, 1 H, iq-CH), 9.14 [d, 1 H, $^3J(\text{H,H}) = 6.5$ Hz, iq-CH], 10.10 (s, 1 H, iq-CH). – ^{13}C NMR (CDCl_3) (100 MHz): $\delta = 18.1$ (tmp-C4), 34.0 (tmp-C7-10), 41.5 (tmp-C3/5), 52.7 (tmp-C2/6), 122.0 (iq-C), 126.8 (iq-C), 127.7 (iq-C), 129.2 (iq-C), 129.5 (iq-C), 134.3 (iq-C), 137.3 (iq-C), 141.1 (iq-C), 155.1 (iq-C). – ^{27}Al NMR (CDCl_3) (70 MHz): $\delta = 102$ ($\Delta_{1/2} = 8300$ Hz). – $\text{C}_{27}\text{H}_{43}\text{AlClN}_3$ (473.10): calcd. C 68.69, H 9.18, N 8.90; found C 67.67, H 8.62, N 8.68.

$\text{tmp}_2\text{AlBr} \cdot \text{iq}$ (3c**):** tmp_2AlBr (40.7 ml, 0.27 M, 11.0 mmol); isoquinoline (2.28 g, 11.0 mmol), yield of **3c**: 5.06 g (89%), m.p. $155–160^\circ\text{C}$. – ^1H NMR (CDCl_3) (400 MHz): $\delta = 1.41$ (t, 8 H, $\text{tmp-}\beta\text{-CH}_2$), 1.37 [s, 24 H, $\text{tmp-C}(\text{CH}_3)_2$], 1.66 (m, 4 H, $\text{tmp-}\gamma\text{-CH}_2$), 7.78 (t, 1 H, iq-CH), 7.94 (m, 3 H, iq-CH), 8.13 (d, 1 H, iq-CH), 9.18 [d, 1 H, $^3J(\text{H,H}) = 7.4$ Hz, iq-CH], 10.17 (s, 1 H, iq-CH). – ^{13}C NMR (CDCl_3) (100 MHz): $\delta = 17.9$ (tmp-C4), 34.1 (tmp-C7-10), 41.5 (tmp-C3/5), 52.9 (tmp-C2/6), 121.8 (iq-C), 126.8 (iq-C), 127.7 (iq-C), 129.4 (iq-C), 129.5 (iq-C), 134.2 (iq-C), 137.5 (iq-C), 141.6 (iq-C), 155.7 (iq-C). – ^{27}Al NMR (CDCl_3) (70 MHz): $\delta = 109$ ($\Delta_{1/2} = 7500$ Hz). – IR (Nujol) [$\nu(\text{Al-Br})$]: $\nu = 332$ cm^{-1} vs. – $\text{C}_{27}\text{H}_{43}\text{AlBrN}_3$ (516.54): calcd. C 62.78, H 8.39, N 8.13, Br 15.5; found C 58.75, H 8.13, N 7.42, Br 15.9.

$\text{tmp}_2\text{AlI} \cdot \text{iq}$ (4b**):** tmp_2AlI (84.9 ml, 0.10 M, 8.5 mmol); isoquinoline (1.76 g, 8.5 mmol), yield of **4b**: 3.93 g (82%), 152°C (decomp. to a black material), m.p. 168°C . – ^1H NMR (CDCl_3) (400 MHz): $\delta = 1.41$ (t, 8 H, $\text{tmp-}\beta\text{-CH}_2$), 1.44 [s, 24 H, $\text{tmp-C}(\text{CH}_3)_2$], 1.65 (m, 4 H, $\text{tmp-}\gamma\text{-CH}_2$), 7.76 (t, 1 H, iq-CH), 7.93 (m, 3 H, iq-CH), 8.15 (d, 1 H, iq-CH), 9.21 [d, 1 H, $^3J(\text{H,H}) = 6.4$ Hz, iq-CH], 10.21 (s, 1 H, iq-CH). – ^{13}C NMR (CDCl_3) (100 MHz): $\delta = 17.7$ (tmp-C4), 34.1 (tmp-C7-10), 41.3 (tmp-C3/5), 53.1 (tmp-C2/6), 121.7 (iq-C), 126.8 (iq-C), 127.5 (iq-C), 129.4 (iq-C), 129.5 (iq-C), 134.0 (iq-C), 137.2 (iq-C), 141.8 (iq-C), 155.3 (iq-C). – ^{27}Al NMR (CDCl_3) (70 MHz): $\delta = 108$ ($\Delta_{1/2} = 8900$ Hz). – IR (Nujol) [$\nu(\text{Al-I})$]: $\nu = 341$ cm^{-1} vs. – $\text{C}_{27}\text{H}_{43}\text{AlIN}_3$ (563.54): calcd. C 57.55, H 7.91, N 7.10, I 22.4; found C 56.55, H 7.69, N 7.46, I 22.5.

$\text{tmp}_2\text{AlBr} \cdot \text{thf}$ (3a**):** tmp_2AlBr (35.1 ml, 0.27 M, 9.5 mmol); THF (5 ml, excess), yield of **3a**: 3.97 g (91%), m.p. $50–53^\circ\text{C}$. – ^1H NMR (C_6D_6) (270 MHz): $\delta = 1.45$ (s, 24 H, tmp-CH_3), 1.31 (t, 8 H, $\text{tmp-}\beta\text{-CH}_2$), 1.58 (m, 4 H, $\text{tmp-}\gamma\text{-CH}_2$), 3.76 (br s, 4 H, $\text{thf-}\alpha\text{-CH}_2$), 1.84 (br s, 4 H, $\text{thf-}\beta\text{-CH}_2$). – ^{13}C NMR (C_6D_6) (100 MHz): $\delta = 18.2$ (tmp-C4), 34.3 (tmp-C7-10), 40.0 (tmp-C3/5), 52.5 (tmp-C2/6), 25.6 ($\text{thf-}\beta\text{-CH}_2$), 68.3 ($\text{thf-}\alpha\text{-CH}_2$). – ^{27}Al NMR (C_6D_6) (70 MHz): $\delta = 125$ ($\Delta_{1/2} = 8080$ Hz). – IR (Nujol) [$\nu(\text{Al-Br})$]: $\nu = 342$ cm^{-1} vs. – $\text{C}_{22}\text{H}_{44}\text{AlBrN}_2\text{O}$ (459.49): calcd. C 57.51, H 9.65, N 6.10, Al 5.9, Br 17.4; found C 56.01, H 9.65, N 5.81, Al 5.4, Br 17.1.

$\text{tmp}_2\text{AlBr} \cdot \text{py}$ (3b**):** tmp_2AlBr (50.0 ml, 0.27 M, 13.5 mmol); pyridine (1.00 g, 13.5 mmol), yield of **3b**: 5.98 g (95%), m.p. $121–125^\circ\text{C}$. – ^1H NMR (C_6D_6) (400 MHz): $\delta = 1.51$ (t, 8 H, $\text{tmp-}\beta\text{-CH}_2$), 1.58 [s, 24 H, $\text{tmp-C}(\text{CH}_3)_2$], 1.74 (m, 4 H, $\text{tmp-}\gamma\text{-CH}_2$), 6.43 (t, 2 H, py-CH), 6.75 (t, 1 H, py-CH), 9.25 (br. s, 2 H, py-CH). – ^{13}C NMR (C_6D_6) (100 MHz): $\delta = 18.6$ (tmp-C4), 34.5

(tmp-C7-10), 42.2 (tmp-C3/5), 53.4 (tmp-C2/6), 124.1 (py-C), 140.4 (py-C), 150.4 (py-C). – ^{27}Al NMR (C_6D_6) (70 MHz): $\delta = 96$ ($\Delta_{1/2} = 4360$ Hz). – IR (Nujol) [$\nu(\text{Al}-\text{Br})$]: $\nu = 347\text{ cm}^{-1}$ vs. – $\text{C}_{23}\text{H}_{41}\text{AlBrN}_3$ (466.48): calcd. C 59.22, H 8.86, N 9.01, Al 5.7, Br 17.2; found C 57.59, H 8.74, N 8.49, Al 5.8, Br 16.5.

tmp₂AlI·py (4a): tmp₂AlI (64.5 ml, 0.10 M, 6.5 mmol); pyridine (0.48 g, 6.5 mmol), yield of **4a**: 3.17 g (95%), m.p. 134–137°C. – ^1H NMR (C_6D_6) (400 MHz): $\delta = 1.48$ (t, 8 H, tmp- β -CH₂), 1.62 [s, 24 H, tmp-C(CH₃)₂], 1.76 (m, 4 H, tmp- γ -CH₂), 6.30 (t, 2 H, py-CH), 6.62 (t, 1 H, py-CH), 9.06 (br s, 2 H, py-CH). – ^{13}C NMR (C_6D_6) (100 MHz): $\delta = 17.8$ (tmp-C4), 34.8 (tmp-C7-10), 42.7 (tmp-C3/5), 53.3 (tmp-C2/6), 125.0 (py-C), 141.9 (py-C), 148.0 (py-C). – ^{27}Al NMR (C_6D_6) (70 MHz): $\delta = 92$ ($\Delta_{1/2} = 4900$ Hz). – $\text{C}_{23}\text{H}_{41}\text{AlIN}_3$ (513.48): calcd. C 53.80, H 8.05, N 8.18, Al 5.3, I 24.7; found C 50.73, H 7.46, N 7.60, Al 5.7, I 25.0.

tmp₂AlI·pic (4c): tmp₂AlI (32.8 ml, 0.10 M, 3.3 mmol); γ -picoline (0.29 g, 3.3 mmol), yield of **4c**: 1.70 g (80%), m.p. 136–139°C. – ^1H NMR (C_6D_6) (400 MHz): $\delta = 1.52$ (t, 8 H, tmp- β -CH₂), 1.66 [s, 24 H, tmp-C(CH₃)₂], 1.73 (m, 4 H, tmp- γ -CH₂), 1.54 (s, 3 H, γ -pic-CH₃), 6.32 (br s, 2 H, β -pic-CH), 9.27 (br s, 2 H, α -pic-CH). – ^{13}C NMR (C_6D_6) (100 MHz): $\delta = 18.3$ (tmp-C4), 34.4 (tmp-C7-10), 42.2 (tmp-C3/5), 53.5 (tmp-C2/6), 125.0 (β -pic-C), 150.2 (α -pic-C). – ^{27}Al NMR (C_6D_6) (70 MHz): $\delta = 77$ ($\Delta_{1/2} = 5900$ Hz). – IR (Nujol) [$\nu(\text{Al}-\text{I})$]: $\nu = 318\text{ cm}^{-1}$ s. – $\text{C}_{24}\text{H}_{43}\text{AlIN}_3$ (527.51): calcd. C 54.65, H 8.22, N 7.39; found C 50.98, H 8.13, N 6.75.

Reaction of tmp₂AlI·py 4a with AgBPh₄ To Give BPh₃·py (5b) and tmp₂AlPh (5a): AgBPh₄ (0.58 g, 1.36 mmol) was suspended in 10 ml of benzene. A solution of tmp₂AlI·py (18.1 ml, 0.075 M, 1.36 mmol) in benzene was added at ambient temperature. The mixture was heated to reflux for 3 days and the insoluble material was filtered off (0.46 g, calcd. AgI: 0.32 g). From the resulting filtrate, all volatiles were removed in vacuo. The residue was extracted with 20 ml of toluene and this solution was stored overnight at –78°C. A microcrystalline precipitate of BPh₃·py (**5b**), (0.17 g, 39%) separated; tmp₂AlPh (**5a**) was characterized in solution by its NMR data^[15].

5b: ^1H NMR (C_6D_6) (270 MHz): $\delta = 7.25$ (t, 3 H, *p*-Ph-H), 7.32 (t, 6 H, *m*-Ph-H), 7.51 (d, 6 H, *o*-Ph-H), 6.15 (br s, 2 H, *m*-py-H), 6.57 (br s, 1 H, *p*-py-H), 8.15 (br s, 2 H, *o*-py-H). – ^{11}B NMR (C_6D_6) (64 MHz): $\delta = 5.1$ (br). – $\text{C}_{23}\text{H}_{20}\text{BN}$ (321.23): calcd. C 86.00, H 6.28, N 4.36; found C 84.20, H 6.61, N 4.28.

tmp₂AlOtos·py (5c): To a suspension of AgOtos (1.00 g, 3.6 mmol) and pyridine (0.29 ml, 3.6 mmol) in 30 ml of toluene, a solution of tmp₂AlBr (13.3 ml, 0.27 M, 3.6 mmol) in *n*-hexane was added at ambient temperature. Immediately, a yellow precipitate of tmp₂AlBr·py separated. The mixture was allowed to stir overnight, and then the insoluble material, which had become somewhat brown, was filtered off and weighed (2.41 g, calcd. AgBr 0.67 g). Extraction with 50 ml of benzene resulted in a yellow solution, which was concentrated in vacuo to a volume of 10 ml. Storage of this solution overnight at 8°C afforded tmp₂AlOtos·py as a colorless precipitate. Yield of **5c**: 0.54 g (28%), decomp. > 311°C. – ^1H NMR (CDCl_3) (270 MHz): $\delta = 1.27$ (t, 8 H, tmp- β -CH₂), 1.09 [br s, 24 H, tmp-C(CH₃)₂], 1.54 (m, 4 H, tmp- γ -CH₂), 2.24 (s, 3 H, toso-CH₃), 7.55 (t, 2 H, *m*-py-H), 7.96 (t, 1 H, *p*-py-H), 9.29 (br s, 2 H, *o*-py-H). – ^{13}C NMR (CDCl_3) (100 MHz): $\delta = 18.1$ (tmp-C4), 33.9 (tmp-C7-10), 40.9 (tmp-C3/5), 52.2 (tmp-C2/6), 21.4 (tos-CH₃), 125.0 (py-C), 141.8 (py-C), 149.8 (py-C), 127.0 (tos-C), 128.3 (tos-C), 128.8 (tos-C), 139.1 (tos-C). – ^{27}Al NMR (C_6D_6) (70 MHz): $\delta = 97$ ($\Delta_{1/2} = 5500$ Hz).

tmp₂Al(lut)(BF₄) (5d): AgBF₄ (1.65 g, 8.5 mmol) and 2,6-lutidine (0.86 g, 8.5 mmol) were suspended in 50 ml of *n*-hexane and

the mixture was cooled to –78°C. A solution of tmp₂AlBr (22.9 ml, 0.35 M, 8.0 mmol) in *n*-hexane was then added slowly and the mixture was allowed to attain ambient temperature. After stirring overnight, the brownish insoluble material was filtered off (2.32 g, calcd. AgBr 1.61 g) and the resulting yellow filtrate was stored for several days at –78°C. Colorless crystals of tmp₂Al(lut)(BF₄) **5d** separated. Yield: 2.47 g (62%); m.p. > 328°C (decomp.). – ^1H NMR (C_6D_6) (400 MHz): $\delta = 1.23$ (t, 8 H, tmp- β -CH₂), 1.06 [s, 24 H, tmp-C(CH₃)₂], 1.53 (m, 4 H, tmp- γ -CH₂), 2.41 (s, 6 H, lut-CH₃), 6.57 (d, 2 H, lut-H), 7.00 (t, 1 H, lut-H). – ^{13}C NMR (C_6D_6) (100 MHz): $\delta = 18.8$ (tmp-C4), 32.0 (tmp-C7-10), 38.6 (tmp-C3/5), 49.6 (tmp-C2/6), 52.4 (lut-CH₃), 119.8 (lut-C), 136.9 (lut-C). – ^{27}Al NMR (C_6D_6) (70 MHz): $\delta = 1$ ($\Delta_{1/2} = 3900$ Hz). – ^{11}B NMR (C_6D_6) (64 MHz): $\delta = 17.9$. – ^{19}F NMR (C_6D_6) (85 MHz): $\delta = -104.5$ (s), -111.0 (s). – IR (Nujol): $\nu = 421$ w, 452 m, 468 s, 507 vs, 527 vs, 551 vs, 568 s, 596 s, 745 w, 762 w, 851 w, 870 w, 900 m, 918 s, 936 vs, 957 vs, 982 vs, 997 vs, 1064 s, 1082 w, 1130 vs, 1180 s, 1202 m, 1236 vs, 1294 w, 1346 m, 1364 s, 1375 s, 1384 s, 1435 m, 1470 s, 1594 w, 1645 w, 1732 w, 2458 w, 2672 w, 2766 w, 2873–3007 vs. – $\text{C}_{25}\text{H}_{45}\text{AlBF}_4\text{N}_3$ (501.44): calcd. C 59.88, H 9.05, N 8.38, Al 5.4; found C 60.06, H 10.07, N 7.47, Al 6.0.

tmp₂Al(py)BF₄ (5e): To a solution of AgBF₄ (1.06 g, 4.96 mmol) in 35 ml of CH₂Cl₂, a solution of tmp₂AlI·py (37.0 ml, 0.134 M, 4.96 mmol) in toluene was added at ambient temperature. Immediately, a dark precipitate formed. After stirring the mixture overnight, the insoluble material was filtered off and the filtrate was concentrated in vacuo. The resulting yellow oil (1.89 g, 80%) was found to be soluble in aliphatic as well as in aromatic or chlorinated solvents. Crystallization could not be achieved. – ^1H NMR (CDCl_3) (270 MHz): $\delta = 0.83$ (t, 8 H, tmp- β -CH₂), 1.23 [s, 24 H, tmp-C(CH₃)₂], 1.60 (m, 4 H, tmp- γ -CH₂), 7.75 (t, 2 H, py-H), 8.22 (t, 1 H, py-H), 8.71 (br s, 2 H, py-H). – ^{27}Al NMR (CDCl_3) (70 MHz): Only an extremely broad, poorly-defined signal was observed. – ^{11}B NMR (CDCl_3) (64 MHz): $\delta = 0.9$; (pentane): $\delta = 19.3$ (no BF coupling observed). – ^{19}F NMR (CDCl_3) (85 MHz): $\delta = -151.0$ [q, $^1J(\text{B},\text{F}) = 12$ Hz]; (pentane): $\delta = -111.0$ (br s).

[tmp₂Al(iq)]AlBr₄ (6a): To a solution of tmp₂AlBr·iq in CH₂Br₂ (33.1 ml, 0.178 M, 5.89 mmol), AlBr₃ (1.57 g, 5.89 mmol) in 10 ml of CH₂Br₂ was added dropwise at 0°C. After 30 min., the clear red solution was reduced to half of its original volume and stored overnight at –20°C. **6a** separated as an orange microcrystalline powder. Yield: 4.43 g (96%), m.p. > 302°C (decomp.). – ^1H NMR (CDCl_3) (270 MHz): $\delta = 1.34$ (t, 8 H, tmp- β -CH₂), 1.47 [s, 24 H, tmp-C(CH₃)₂], 1.62 (m, 4 H, tmp- γ -CH₂), 7.94 (t, 1 H, iq-CH), 8.10 (m, 2 H, iq-CH), 8.28 (d, 1 H, iq-CH), 8.30 (d, 1 H, iq-CH), 8.94 [d, 1 H, $^3J(\text{H},\text{H}) = 6.4$ Hz, iq-CH], 9.89 (s, 1 H, iq-CH). – ^{13}C NMR (CDCl_3) (100 MHz): $\delta = 17.5$ (tmp-C4), 34.2 (tmp-C7-10), 39.9 (tmp-C3/5), 52.5 (tmp-C2/6), 124.2 (iq-C), 127.0 (iq-C), 127.5 (iq-C), 130.1 (iq-C), 130.1 (iq-C), 136.4 (iq-C), 137.1 (iq-C), 137.7 (iq-C), 152.5 (iq-C). – ^{27}Al NMR (CDCl_3) (70 MHz): $\delta = 102$ ($\Delta_{1/2} = 66$ Hz); (CH₂Br₂): $\delta = 104$ ($\Delta_{1/2} = 53$ Hz). – IR (Nujol) [$\nu(\text{Al}-\text{Br})$]: $\nu = 429\text{ cm}^{-1}$ vs. – $\text{C}_{27}\text{H}_{43}\text{Al}_2\text{Br}_4\text{N}_3$ (783.24): calcd. C 41.40, H 5.53, N 5.36, Al 6.9, Br 40.8; found C 36.01, H 5.12, N 4.43, Al 7.2, Br 40.7 (C, H, N ratio: calcd. 9:14.33:1; found 9.48:16.06:1).

[tmp₂Al(py)]AlI₄ (6b): To AlI₃ (0.62 g, 1.5 mmol) dissolved in 5 ml of benzene, a solution of tmp₂AlI·py (20.0 ml, 0.075 M, 1.5 mmol) in benzene was added at ambient temperature. The mixture was stirred overnight. Subsequent addition of 5 ml of pentane led to the precipitation of yellowish **6b**. Yield: 1.10 g (79%), decomp. at $T > 166^\circ\text{C}$ (blackens). – ^1H NMR (C_6D_6) (270 MHz): $\delta = 1.31$ (t, 8 H, tmp- β -CH₂), 1.48 [s, 24 H, tmp-C(CH₃)₂], 1.55 (m, 4 H,

tmp- γ -CH₂), 6.21 (t, 2 H, py-CH), 6.57 (t, 1 H, py-CH), 8.59 (br s, 2 H, py-CH). – ¹³C NMR (C₆D₆) (100 MHz): δ = 18.1 (tmp-C4), 34.5 (tmp-C7-10), 40.2 (tmp-C3/5), 52.9 (tmp-C2/6), 125.5 (py-C), 142.2 (py-C), 147.0 (py-C). – ²⁷Al NMR (C₆D₆) (70 MHz): δ = 50 ($\Delta_{1/2}$ = 134 Hz). – IR (Nujol) [ν (Al–I)]: ν = 338 cm^{–1} vs. – C₂₃H₄₁AlI₂N₃ (921.18): calcd. C 29.99, H 4.49, N 4.56, Al 5.9, I 55.1; found C 29.55, H 4.62, N 3.67, Al 5.8, I 55.6.

[tmp₂Al(4-Me-py)]AlI₄ (**6c**): To a solution of tmp₂AlI (50 ml, 0.10 M, 5.0 mmol) in *n*-hexane, γ -picoline (0.50 ml, 5.0 mmol) was added at ambient temperature. From the resulting suspension, all volatiles were removed in vacuo. The residue was redissolved in 50 ml of diethyl ether and the solution was cooled to –78°C. After the addition of AlI₃ powder (2.04 g, 5.0 mmol), the mixture was allowed to warm to ambient temperature (1.5 h). The cloudy solution was filtered and the filtrate was concentrated to a volume of 25 ml. At this stage, the NMR spectra of **6c** were recorded by removal of all volatiles from a portion of the solution in vacuo and redissolving the residue in C₆D₆. Storage of the filtrate for several weeks at –78°C afforded colorless crystals of tmp₂AlI **1c** (2.07 g, 95%) (characterized by its NMR spectra and check of the unit cell parameters)^[15].

6c: ¹H NMR (C₆D₆) (270 MHz): δ = 1.29 (t, 8 H, tmp- β -CH₂), 1.46 [s, 24 H, tmp-C(CH₃)₂], 1.56 (m, 4 H, tmp- γ -CH₂), 1.49 (s, 3 H, γ -pic-CH₃), 6.12 (d, 2 H, γ -pic-CH), 8.47 (br s, 2 H, γ -pic-CH). – ¹³C NMR (C₆D₆) (100 MHz): δ = 18.1 (tmp-C4), 34.5 (tmp-C7-10), 40.0 (tmp-C3/5), 52.8 (tmp-C2/6), 21.3 (γ -pic-CH₃), 126.5 (γ -pic-C), 145.9 (γ -pic-C), 156.9 (γ -pic-C). – ²⁷Al NMR (C₆D₆) (70 MHz): δ = 51 ($\Delta_{1/2}$ = 35 Hz).

[tmp₂Al(4-*t*Bu-py)]AlI₄ (**6d**): To a solution of tmp₂AlI (25 ml, 0.10 M, 2.5 mmol) in *n*-hexane, 4-*t*Bu-py (0.36 ml, 2.5 mmol) was added at ambient temperature. From the resulting suspension of tmp₂AlI·4-*t*Bu-py, all volatiles were removed in vacuo and the yellow residue was redissolved in 35 ml of toluene. AlI₃ powder (1.01 g, 2.5 mmol) was then added in one portion. The mixture was stirred for 1 h, then the cloudy solution was filtered. After concentration of the filtrate to one-third of its original volume, the solution was cooled to –78°C. NMR spectra of **6d** were obtained from this solution. Even after weeks at various temperatures and at different concentrations, no crystals suitable for X-ray structure determination were formed. – ¹H NMR (C₆D₆) (270 MHz): δ = 1.28 (t, 8 H, tmp- β -CH₂), 1.45 [s, 24 H, tmp-C(CH₃)₂], 1.56 (m, 4 H, tmp- γ -CH₂), 0.69 (s, 9 H, *t*Bu-CH₃), 6.35 (d, 2 H, 4-*t*Bu-py-CH), 8.54 (br s, 2 H, 4-*t*Bu-py-CH). – ¹³C NMR (C₆D₆) (100 MHz): δ = 18.1 (tmp-C4), 34.4 (tmp-C7-10), 40.0 (tmp-C3/5), 52.8 (tmp-C2/6), 29.5 (4-*t*Bu-CH₃), 127.8 (4-*t*Bu-py-C), 146.6 (4-*t*Bu-py-C), 156.9 (4-*t*Bu-py-C). – ²⁷Al NMR (C₆D₆) (70 MHz): δ = 51 ($\Delta_{1/2}$ = 74 Hz).

[tmp₂Al(iq)]AlI₄ (**6e**): To tmp₂AlI-iq (1.71 g, 3.03 mmol) dissolved in 15 ml of toluene, a solution of AlI₃ (1.24 g, 3.03 mmol) in 10 ml of toluene was added at a temperature of 5–10°C. After stirring for 1.5 h, the mixture was filtered and the clear filtrate was concentrated to dryness in vacuo. A reddish-brown residue of [tmp₂Al(iq)]AlI₄ was obtained. Yield: 2.91 g (99%); m.p. > 330°C (decomp.). – ¹H NMR (CDCl₃) (270 MHz): δ = 1.32 (t, 8 H, tmp- β -CH₂), 1.41 [s, 24 H, tmp-C(CH₃)₂], 1.61 (m, 4 H, tmp- γ -CH₂), 7.91 (t, 1 H, iq-CH), 8.08 (m, 2 H, iq-CH), 8.14 (d, 1 H, iq-CH), 8.26 (d, 1 H, iq-CH), 8.75 [d, 1 H, ³J(H,H) = 8.4 Hz, iq-CH], 9.70 (s, 1 H, iq-CH). – ¹³C NMR (CDCl₃) (100 MHz): δ = 17.6 (tmp-C4), 34.0 (tmp-C7-10), 39.5 (tmp-C3/5), 52.0 (tmp-C2/6), 124.4 (iq-C), 127.1 (iq-C), 127.7 (iq-C), 130.1 (iq-C), 130.8 (iq-C), 136.4 (iq-C), 137.0 (iq-C), 137.9 (iq-C), 152.4 (iq-C). – ²⁷Al NMR (CDCl₃) (70 MHz): δ = 55 ($\Delta_{1/2}$ = 17 Hz); (CH₂Cl₂): δ = 54 ($\Delta_{1/2}$ = 43

Hz). – IR (Nujol) [ν (Al–I)]: $\tilde{\nu}$ = 362 cm^{–1} vs. – C₂₇H₄₃AlI₂N₃ (783.24): calcd. C 33.39, H 4.46, N 4.33, Al 5.6, I 52.3; found C 35.54, H 4.97, N 3.98, Al 5.2, I 52.8 (C,H ratio: calcd. 1:1.59; found 1:1.65).

[tmp₂Al(acr)]AlI₄ (**6f**): To a solution of tmp₂AlI (0.81 g, 1.84 mmol) in 50 ml of CH₂Cl₂, a solution of acridine (8.80 ml, 0.209 M, 1.84 mmol) in CH₂Cl₂ was added at –78°C. The mixture was kept at this temperature for 1 h and then 0.75 g (1.84 mmol) of AlI₃ was added in one portion. The suspension was slowly allowed to warm to ambient temperature and then filtered. From the orange-red filtrate, all volatiles were removed in vacuo. The residue was characterized as **6f** (1.86 g, 99%). Attempts to crystallize the product from various solvents were not successful. – ¹H NMR (CDCl₃) (270 MHz): δ = 1.34 (t, 8 H, tmp- β -CH₂), 1.47 [s, 24 H, tmp-C(CH₃)₂], 1.65 (m, 4 H, tmp- γ -CH₂), 7.53 (t, 2 H, acr-CH), 7.78 (t, 2 H, acr-CH), 8.01 (d, 2 H, acr-CH), 8.21 (d, 2 H, acr-CH), 8.80 (s, 1 H, acr-CH). – ¹³C NMR (CDCl₃) (100 MHz): δ = 17.7 (tmp-C4), 34.3 (tmp-C7-10), 39.8 (tmp-C3/5), 52.6 (tmp-C2/6), 125.8 (acr-C), 126.6 (acr-C), 128.3 (acr-C), 128.8 (acr-C), 136.6 (acr-C), 148.7 (acr-C). – ²⁷Al NMR (CDCl₃) (70 MHz): δ = –22 ($\Delta_{1/2}$ = 70 Hz); (CH₂Cl₂): δ = –27 ($\Delta_{1/2}$ = 65 Hz). – C₃₁H₄₅AlI₂N₃ (1021.28): calcd. Al 5.3, I 49.7; found Al 5.1, I 50.0.

AlBr₃·acr (**7a**): To a solution of tmp₂AlBr (50 ml, 0.12 M, 6.0 mmol) in *n*-hexane, a solution of acridine (4.88 ml, 1.23 M, 6.0 mmol) in toluene was added at ambient temperature. After the addition of AlBr₃ (1.60 g, 6.0 mmol), a greenish-yellow precipitate of AlBr₃·acr formed immediately. The insoluble material was filtered off and washed twice with pentane. Yield: 2.40 g (90%); decomp. at *T* > 186°C. – The ²⁷Al-NMR spectrum of the filtrate exhibited the chemical shift of tmp₂AlBr (**1b**) ($d^{27}\text{Al}$ = 130; $\Delta_{1/2}$ = 10200 Hz)^[15]. – ¹H NMR (CDCl₃) (270 MHz): δ = 7.68 (t, 2 H, acr-H), 7.96 (t, 2 H, acr-H), 8.16 (d, 2 H, acr-H), 8.45 (br d, 2 H, acr-H), 9.14 (s, 1 H, acr-H). – ²⁷Al NMR (CDCl₃) (70 MHz): δ = 83 ($\Delta_{1/2}$ = 38 Hz). – IR (Nujol) [ν (Al–Br)]: ν = 404 cm^{–1} vs. 460 vs. – C₁₃H₉AlBr₃N (379.68): calcd. C 35.02, H 2.03, N 3.14; found C 35.59, H 3.18, N 3.28.

AlI₃·4-*t*Bu-py (**7b**): A solution of tmp₂AlI (51.5 ml, 0.10 M, 5.15 mmol) in *n*-hexane was diluted with a further 150 ml of the solvent. Then, 4-*t*Bu-py (0.75 ml, 5.15 mmol) was added. To this clear solution, powdered AlI₃ (2.10 g, 5.15 mmol) was added at ambient temperature. On leaving the mixture to stand overnight, a copious amount of a colorless precipitate was deposited, which was removed by filtration. Washing the solid with pentane afforded (2.70 g, 96%) of **7b**, m.p. 154–158°C (becomes red). NMR analysis of the filtrate showed only the signals of **1c**. – ¹H NMR (C₆D₆) (400 MHz): δ = 0.65 [s, 9 H, *t*Bu-C(CH₃)₃], 6.42 (t, 2 H, py-CH), 8.63 (d, 2 H, py-CH). – ¹³C NMR (C₆D₆) (100 MHz): δ = 29.3 [*t*Bu-C(CH₃)₃], 35.1 [*t*Bu-C(CH₃)₃], 122.9 (py-C), 146.6 (py-C). – ²⁷Al NMR (C₆D₆) (70 MHz): δ = 51 ($\Delta_{1/2}$ = 46 Hz). – IR (Nujol) [ν (Al–I)]: ν = 371 cm^{–1} vs. 385 vs. – C₉H₁₃AlI₃N (542.89): calcd. C 19.91, H 2.41, N 2.58; found C 21.08, H 2.88, N 2.63.

tmpAlI₂·py (**7c**): To a solution of tmp₂AlI·py (28.7 ml, 0.134 M, 3.85 mmol) in toluene, AlI₃ (1.57 g, 3.85 mmol) was added at 0°C and the mixture was kept stirring overnight. The turbid solution was then filtered and the filtrate was concentrated to dryness in vacuo. The resulting brownish oil was stored for some days at temperatures up to 35°C. After one week, colorless crystals of **7c** formed. These were isolated from the oil (1.70 g, 88%) and washed twice with pentane; m.p. > 202°C (decomp.). – ¹H NMR (C₆D₆) (400 MHz): δ = 1.39 (t, 4 H, tmp- β -CH₂), 1.63 [s, 12 H, tmp-C(CH₃)₂], 1.60 (m, 2 H, tmp- γ -CH₂), 6.26 (t, 2 H, py-CH), 6.59 (t, 1 H, py-CH), 9.05 (br s, 2 H, py-CH). – ¹³C NMR (C₆D₆) (100

Table 6. Crystallographic data and details relating to the data collection and structure solution of the compounds examined by X-ray diffraction analysis

Compound	tmp ₂ AlCl·iq 2a	tmp ₂ AlCl·thf 2b	tmp ₂ AlBr·thf 3a	tmp ₂ AlBr·py 3b	tmp ₂ AlI·py 4a	AlI ₃ ·iq 7b	tmpAlI ₂ ·py 7c
Chem. formula	C ₂₇ H ₄₃ AlClN ₃	C ₂₂ H ₄₄ AlClN ₂ O	C ₂₂ H ₄₄ AlBrN ₂ O	C ₂₃ H ₄₁ AlBrN ₃	C ₂₃ H ₄₀ AlIN ₃	C ₉ H ₇ AlI ₃ N	C ₁₄ H ₂₃ AlI ₂ N ₂
Form wght.	472.07	415.02	459.48	466.48	512.46	536.84	500.12
Cryst. size [mm]	0.4 × 0.5 × 0.5	0.2 × 0.3 × 0.3	0.4 × 0.3 × 0.3	0.6 × 0.4 × 0.4	0.2 × 0.2 × 0.3	0.1 × 0.1 × 0.3	0.7 × 0.5 × 0.4
Cryst. system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	10.685(3)	7.715(3)	8.104(3)	31.700(1)	32.21(1)	20.01(3)	9.861(3)
<i>b</i> [Å]	16.945(1)	18.396(6)	16.986(6)	11.086(5)	11.063(6)	10.23(1)	18.133(1)
<i>c</i> [Å]	14.745(5)	17.139(6)	17.576(9)	14.671(6)	14.886(8)	14.12(2)	10.113(4)
α [°]	90	90	90	90	90	90	90
β [°]	100.83(2)	94.444(5)	98.62(4)	108.64(3)	110.394(1)	107.27(5)	99.41(3)
γ [°]	90	90	90	90	90	90	90
<i>V</i> [Å ³]	2622.0(2)	2425.0(2)	2392.1(2)	4885.3(3)	4971.2(4)	2759(7)	1784.0(1)
<i>Z</i>	4	4	4	8	8	8	4
ρ_{calcd} [Mg/m ³]	1.196	1.137	1.276	1.268	1.369	2.585	1.862
μ [mm ⁻¹]	0.199	0.208	1.769	1.732	1.337	6.828	3.566
absol.	—	—	—	—	semiempirical	semiempirical	semiempirical
min./max. transm.	—	—	—	—	0.621 and 0.851	0.144 and 1.000	0.055, 0.107
<i>F</i> (000)	1024	912	984	1984	2120	1920	960
Index range	0 ≤ <i>h</i> ≤ 12 0 ≤ <i>k</i> ≤ 19 −16 ≤ <i>l</i> ≤ 16	−9 ≤ <i>h</i> ≤ 9 −23 ≤ <i>k</i> ≤ 21 −21 ≤ <i>l</i> ≤ 22	5 ≤ <i>h</i> ≤ 0 0 ≤ <i>k</i> ≤ 19 −19 ≤ <i>l</i> ≤ 19	−35 ≤ <i>h</i> ≤ 0 0 ≤ <i>k</i> ≤ 12 −15 ≤ <i>l</i> ≤ 16	−35 ≤ <i>h</i> ≤ 35 −13 ≤ <i>k</i> ≤ 13 −18 ≤ <i>l</i> ≤ 18	−24 ≤ <i>h</i> ≤ 24 −12 ≤ <i>k</i> ≤ 12 −17 ≤ <i>l</i> ≤ 17	−11 ≤ <i>h</i> ≤ 11 −3 ≤ <i>k</i> ≤ 21 −4 ≤ <i>l</i> ≤ 12
2 θ [°]	48.00	58.14	47.10	47.12	54.76	54.78	50.06
Temp. [K]	233	173	223	213(2)	213	213	223
Refl. collected	4267	13580	2899	3709	13202	7175	3081
Refl. unique	4030	4752	2618	3636	3735	2684	2948
Refl. observed (4 σ)	2191	4159	2042	2581	3291	1561	2667
<i>R</i> _{int}	0.0826	0.0416	0.0383	0.0614	0.0725	0.0832	0.0868
No. variables	297	252	252	261	261	127	176
Weighting scheme	0.0841/12.9220	0.0225/3.8906	0.1000/0.0000	0.0539/9.6308	0.0622/13.5922	0.1334/18.0998	0.0783/ 5.0904
χ^2_{red} ^[a]	—	—	—	—	—	—	—
GooF	1.025	1.214	1.169	1.034	1.144	1.152	1.088
Final <i>R</i> (4 σ)	0.0915	0.0669	0.0479	0.0495	0.0474	0.0669	0.0457
Final <i>wR</i> ₂	0.2043	0.1332	0.1467	0.1050	0.1116	0.1756	0.1241
Larg. res. peak [e/Å ³]	0.894	0.577	0.658	0.768	0.885	2.760	1.785

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

MHz): δ = 17.6 (tmp-C4), 34.8 (tmp-C7-10), 42.7 (tmp-C3/5), 53.3 (tmp-C2/6), 124.9 (py-C), 141.7 (py-C), 148.0 (py-C). — ²⁷Al NMR (C₆D₆) (70 MHz): δ = 69 ($\Delta_{1/2}$ = 2640 Hz). — IR (Nujol) [ν (Al—I)]: ν = 315 cm⁻¹ vs, 335 vs, 355 vs. — C₁₄H₂₃AlI₂N₂ (500.14): calcd. C 33.62, H 4.64, N 4.80; found C 33.40, H 4.80, N 5.13.

X-ray Crystal Structure Determinations: Data collection for X-ray structure determinations was performed on a Syntex P4 or a Syntex R3 four-circle diffractometer using graphite-monochromated Mo-*K*_α (λ = 0.71073 Å) radiation. Single crystals were mounted in Lindemann capillaries and sealed under argon atmosphere. Other data collection for X-ray structure determinations was performed on a Siemens P4 four-circle diffractometer equipped with a CCD area detector^[32]. Single crystals were mounted in polyfluoroether oil and fixed on top of a glass fibre. Data was collected at −80 to −100 °C. All calculations were performed on PC's and workstations using the Siemens SHELXTL-Plus^[33] or SHELX-93^[34] software packages. The structures were solved by direct or heavy atom methods and successive interpretation of the difference Fourier maps, followed by least-squares refinement. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the refinement in calculated positions by a riding model using fixed isotropic thermal parameters. Data relevant to the crystallography, data collection and refinement are compiled in Table 6. Further details of the crystal structure determinations are deposited at the Cambridge Crystallographic Data Centre and may

be requested by quoting the depository number CSD-101038, the names of the authors, and the full journal citation.

- [1] I. Krossing, Dissertation, University of Munich, **1997**.
- [2] Responsible for some X-ray crystal structure determinations.
- [3] J. D. Smith, I. J. Worrall, A. McKillop, *Dictionary of Organometallic Compounds*, Chapman and Hall, London **1984–1989**, *Aluminum* pp. 9–120, *Gallium* pp. 940–962, *Indium* pp. 1138–1151.
- [4] A. Haaland, *Angew. Chem.* **1989**, *101*, 1017–1032; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 992.
- [5] [5a] P. Pullmann, K. Hensen, J. W. Bats, *Z. Naturforsch. Part B* **1982**, *37*, 1312–1316. — [5b] D. M. Brown, D. T. Stewart, D. E. H. Jones, *Spectrochim. Acta* **1973**, *29a*, 213–217. — [5c] M. Dalibart, J. Derouault, M. T. Forel, *J. Mol. Struct.* **1981**, *70*, 119–123. — [5d] I. R. Beattie, P. J. Jones, J. A. K. Howard, L. E. Smart, C. J. Gilmore, J. W. Akitt, *J. Chem. Soc., Dalton Trans.* **1979**, 528–541. — [5e] J. Meunier, M. T. Forel, *Can. J. Chem.* **1972**, *50*, 1157–1161.
- [6] [6a] A. J. Downs (Ed.), *Chemistry of Aluminium, Gallium, Indium and Thallium*, Blackie Academic and Professional, London, **1993**. — [6b] N. N. Greenwood, K. Wade, *Friedel-Crafts and Related Reactions* (Ed.: G. Olah), Interscience, New York, **1963**.
- [7] P. J. Olgren, J. P. Cannon, C. F. Smith Jr., *J. Phys. Chem.* **1971**, *75*, 282–289.
- [8] L. Jakobsmeier, I. Krossing, H. Nöth, M. J. H. Schmidt, *Z. Naturforsch. Part B* **1996**, *51*, 1117–1126.
- [9] H. Nöth, R. Rurländer, P. Wolfgardt, *Z. Naturforsch. Part B* **1982**, *37*, 29–35.
- [10] D. A. Atwood, J. Jegler, *Inorg. Chem.* **1996**, *35*, 4277–4282.

- [11] W. Uhl, J. Wagner, D. Fenske, G. Baum, *Z. anorg. allg. Chem.* **1992**, 612, 25–33.
- [12] U. Kynast, B. W. Skelton, A. H. White, M. J. Henderson, C. L. Raston, *J. Organomet. Chem.* **1990**, 384, C1.
- [13] K. Ruhlandt-Senge, P. P. Power, *Inorg. Chem.* **1991**, 30, 2633–2639.
- [14] M. G. Gardiner, M. G. Koutsantonis, S. M. Lawrence, F.-C. Lee, C. L. Raston, *Chem. Ber.* **1996**, 129, 545–549.
- [15] I. Krossing, H. Nöth, C. Tacke, M. Schmidt, H. Schwenk, *Chem. Ber.* **1997**, 130, 1047–1052.
- [16] I. Krossing, H. Nöth, B. N. Anand, *Inorg. Chem.* **1997**, 36, 1979–1981.
- [17] K. Knabel, I. Krossing, H. Nöth, H. Schwenk-Kircher, M. J. H. Schmidt-Amelunxen, T. Seifert, unpublished results.
- [18] Low local symmetry leads to broad signals and vice versa. See refs. [19a] and [19b].
- [19] [19a] J. Mason, *Multinuclear NMR*, Plenum Press, New York and London, **1987**, 259–278. – [19b] H. Lehmkuhl, *J. Organomet. Chem.* **1991**, 411, 37–55.
- [20] H. Nöth, B. Wrackmeyer, *NMR Spectroscopy of Boron Compounds*, Vol. 14 (Eds.: P. Diehl, E. Fluck, R. Korfeld), Springer Verlag, Berlin, Heidelberg, New York, **1978**.
- [21] $\text{BPh}_3 \cdot \text{py}$ (**5b**) precipitates in triclinic crystals of space group $P1$ ($Z = 2$) from benzene/pentane solutions. As the B–N and C–C bonds are isoelectronic, the pyridine and phenyl ligands are site disordered, so that every phenyl position is occupied to 1/4 by the pyridine molecule. Therefore, bond lengths cannot be discussed, but the structure is an additional proof for the reaction described by Eq. 2b.
- [22] R. M. Fuoss, C. A. Kraus, *J. Am. Chem. Soc.* **1933**, 55, 2387–2399.
- [23] V. Shomaker, D. P. Stevenson, *J. Am. Chem. Soc.* **1941**, 63, 37–40.
- [24] R. J. Wehmschulte, W. J. Grigsby, B. Schiemenz, R. A. Bartlett, P. P. Power, *Inorg. Chem.* **1996**, 35, 6694–6702.
- [25] I. Krossing, Dissertation, University of Munich, **1997**.
- [26] M. A. Petrie, P. P. Power, H. V. Rasika Dias, K. Ruhlandt-Senge, K. M. Waggoner, R. J. Wehmschulte, *Organometallics* **1993**, 12, 1086–1093.
- [27] M. J. Zaworotko, J. L. Atwood, *Inorg. Chem.* **1980**, 19, 268–271.
- [28] J. L. Atwood, P. A. Milton, *J. Organomet. Chem.* **1973**, 52, 275–279.
- [29] Performed with the program *Hyperchem*, V3.0, Autodesk, **1993**.
- [30] Performed with the program *Gaussian 94*, Revision B.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1995**.
- [31] S. H. Strauss, *Chem. Rev.* **1993**, 93, 927–942.
- [32] Siemens Industrial Automation, **1995**.
- [33] *PC SHELXTL Rel. 5.03*, Siemens Analytical Instruments, Version 4.1, **1994**.
- [34] G. M. Sheldrick, University of Göttingen, **1993**.

[97292]