Adducts of Aluminum and Gallium Trichloride with a *N*-Heterocyclic Carbene and an Adduct of Aluminum Trichloride with a Thione

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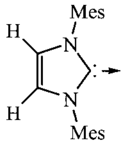
The reactions of $AlCl_3$ and $GaCl_3$ with 1,3,4,5-tetramethylimidazole-2-ylidene in toluene at room temperature affords the 1:1 adducts **5** and **6**, respectively. The use of a bulky *N*-heterocyclic carbene (NHC) in toluene/THF and $AlCl_3$ results in the formation of an imidazolium salt **7** with the tetrachloroaluminate anion. A 1:1 adduct **8** of 1,3,4,5-tetramethylimidazole-2(3*H*)-thione with $AlCl_3$ is obtained in toluene. The crystal structures of $\mathbf{5}\cdot0.5C_7H_8$, $\mathbf{7}\cdot$THF and **8** were determined.

Introduction

The use of *N*-heterocyclic carbenes (NHC)[1,2] as good σ-donor molecules to stabilize trivalent group 13 compounds was established with the isolation of the first alane adduct of an imidazol-2-ylidene **1**.[3] The stability of these complexes is demonstrated by the melting point of **1** (246−247 °C). Compound **1** melts without decomposition, whereas $AlH_3\cdot NMe_3$ decomposes above 100 °C.[4] The properties of the corresponding gallium and indium compounds allow their isolation and characterization.[5,6] However, adducts of a NHC with aluminum or gallium halides have not been reported. The reaction of a bidentate NHC ligand with $AlCl_3$ in diethyl ether resulted in an imidazolium salt in moderate yield and in by-products, although moisture was excluded from the reaction mixture.[7] Only adducts of a phosphanylsilylcarbene with MCl_3 (M = Al **2**, Ga **3**, In **4**) were reported and the X-ray single-crystal structure of **3** was determined.[8] From reactions of a NHC with InX_3 (X = Cl, Br) under different conditions, carbene adducts with a composition of 1:1 and 1:2 ratios as well as imidazolium salts of carbene-stabilized indates were obtained and structurally characterized.[9]



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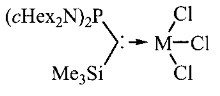
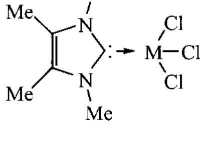


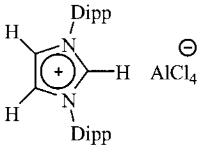
M = Al **2**
= Ga **3**
= In **4**

Results and Discussion

$AlCl_3$ was treated with one equivalent of 1,3,4,5-tetramethylimidazole-2-ylidene[10] in toluene at room temperature; $AlCl_3$ dissolved after 30 minutes. The mixture was filtered and concentrated. Colorless plates of **5** were obtained in 56% yield at low temperature. The ^1H NMR spectrum of **5** shows two singlets (δ = 1.15 and δ = 3.23 ppm) for the protons of the methyl groups of the carbene ligand. They are shifted upfield relative to the free carbene 1,3,4,5-tetramethylimidazole-2-ylidene (δ = 1.59 and δ = 3.35 ppm). No resonances for an imidazolium salt were detected. A weak and broad ^{13}C NMR resonance (δ = 154 ppm) can be assigned to the carbene carbon atom. The ^{27}Al NMR spectrum shows a resonance at δ = 103 ppm, which is typical for four-coordinate aluminum and in the region of the resonances for hydride derivatives. EI mass spectrometry presents a molecular ion peak at *m*/*z* = 256 in the correct isotopic pattern and free 1,3,4,5-tetramethylimidazole-2-ylidene as the base peak. Compound **5** crystallizes with half a molecule of toluene in the triclinic space group $P\bar{1}$. It exhibits the expected assembly (see Figure 1), and selected bond lengths and angles are given in Table 1. The Al−C distance in **5** is 2.009(5) Å, which is shorter than the corresponding bond length in the adduct of 1,3,4,5-tetra-



M = Al **5**
= Ga **6**



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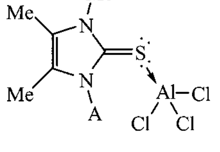

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methylimidazole-2-ylidene with Al(C≡C*t*Bu)$_3$ [2.051(2) Å].[11]

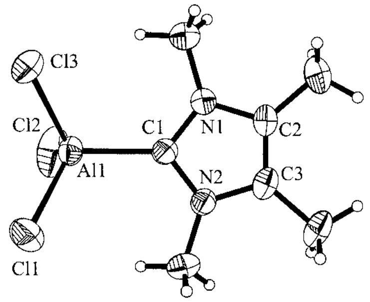

Figure 1. Crystal structure of **5**·0.5C$_7$H$_8$; toluene omitted for clarity

Table 1. Selected bond lengths (Å) and angles (°) of **5**·0.5C$_7$H$_8$

Al1−C1	2.009(5)	Al1−Cl1	2.134(4)
Al1−Cl2	2.121(5)	Al1−Cl3	2.131(3)
N1−C1	1.352(5)	N1−C2	1.392(5)
N2−C1	1.353(5)	N2−C3	1.387(5)
C2−C3	1.343(6)		
C1−Al1−Cl1	111.1(2)	Cl2−Al1−Cl1	110.43(17)
N2−C1−N1	104.8(3)	C3−C2−N1	106.9(4)

The gallium analogue of **5** could be prepared and crystallized by a comparable method in 62% yield. Due to the dimeric nature of GaCl$_3$ and its good solubility in hydrocarbon solvents, in contrast to polymeric AlCl$_3$ in the solid state, GaCl$_3$ was cooled with liquid nitrogen while a solution of 1,3,4,5-tetramethylimidazole-2-ylidene in toluene was added, and the mixture was slowly warmed to room temperature. No single crystals were obtained for **6** but the ^{1}H NMR spectrum shows a ratio of ca.1:0.70 ratio of **6** and toluene. The GaCl$_3$ adduct **6** is less soluble than **5**. The resonances for the methyl groups (δ = 1.05 and 3.19 ppm) are in the region of the resonances for **5**. A resonance for the carbene carbon atom was not observed in the ^{13}C NMR spectrum, as seen before for comparable compounds.[7,9] The EI mass spectrum shows the molecular ion peak M$^+$ at *m*/*z* = 300 with the expected isotopic pattern as well as M$^+$ − Cl at *m*/*z* = 265. A gallium triiodide adduct of a NHC was very recently prepared in our group from the corresponding hydride and was structurally characterized.[12] The computed M−C distance for the adduct of MCl$_3$ (M = Al, Ga) with diaminocarbene are 2.060 Å for Al and 2.079 Å for Ga.[13] These bond lengths are nearly identical. We also found a very similar bond length for the carbene adduct of Ga(C≡C*t*Bu)$_3$ with 1,3,4,5-tetramethylimidazole-2-ylidene [2.057(3) Å][14] and the corresponding aluminum compound [2.051(2) Å, see above]. The Ga−C bond length in **3** is 1.978(10) Å.

The reaction of a bulky imidazolylidene with AlCl$_3$ in THF/toluene afforded the imidazolium salt **7**·THF in moderate yield (Figure 2). The very poorly soluble compound **7**·THF was characterized by an X-ray single-crystal structure determination. Selected bond lengths and angles are summarized in Table 2. Only the cationic species for the corresponding imidazolium salt could be detected in the FAB mass spectrum at (*m*/*z* = 389), and no peak for the tetrachloroaluminate anion was observed. However, the EI-mass spectrum of the salt shows the ions for the corresponding AlCl$_3$ carbene adduct with one chlorine less (*m*/*z* = 484) and with only one chlorine (*m*/*z* = 451) in the expected isotopic pattern. It is known that AlCl$_3$ dissociates in THF[15,16] and other donor solvents[17,18] to form donor-stabilized salts of the type [AlCl$_2$(Do)$_x$][AlCl$_4$]. Moreover, we assume that the hydrogen atoms in the backbone (here on C2 and C3) of the imidazolylidene are responsible for the protonation and the formation of the imidazolium salt.

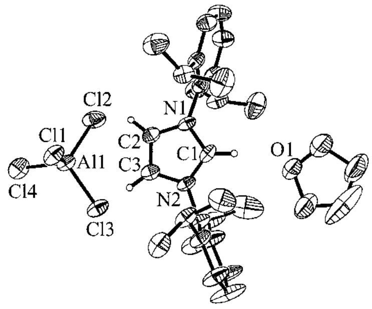

Figure 2. Crystal structure of **7**·THF; only hydrogen atoms on the imidazolium ring are shown

Table 2. Selected bond lengths (Å) and angles (°) of **7**·THF

Al1−Cl2	2.129(2)	Al1−Cl3	2.140(2)
C1−N1	1.334(6)	C1−N2	1.322(7)
N1−C2	1.379(7)	N2−C3	1.391(6)
Cl1−Al1−Cl2	109.34(10)	N2−C1−N1	108.6(4)

In a comparable route, 1,3,4,5-tetramethylimidazole-2(3*H*)-thione, which is a common starting material for the preparation of 1,3,4,5-tetramethylimidazole-2-ylidene by reduction with potassium in THF,[10] reacts with AlCl$_3$ in toluene to afford adduct **8** (Figure 3). The latter compound is less soluble than **5**. The ^{1}H NMR resonances of the ligand exhibit singlets at δ = 1.27 and δ = 3.12 ppm. Only the free thione was detected by EI mass spectrometry. Compound **8** crystallizes in the orthorhombic space group *Pbca*. Selected bond lengths and angles are given in Table 3. The Al−S bond length is 2.2661(13) Å. The C=S bond length

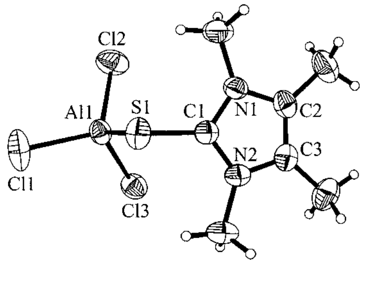

Figure 3. Crystal structure of **8**

in the free thione [1.690(2) Å][19] is elongated upon coordination with $AlCl_3$ in **8** [1.739(3) Å] by nearly 0.05 Å. The $AlCl_3$ moiety is coordinated to one lone pair of the sulfur atom to give a C1−S1−Al1 angle of 98.79(9)°. The adduct **8** is a model compound for the activation of a carbonyl function by a Lewis acid.

Table 3. Selected bond lengths (Å) and angles (°) of **8**

Al1−Cl1	2.1242(12)	Al1−Cl2	2.1300(13)
Al1−Cl3	2.1318(12)	Al1−S1	2.2661(13)
S1−C1	1.739(3)	C1−N1	1.347(4)
C1−N2	1.338(4)	N1−C2	1.399(4)
N2−C3	1.391(4)	C2−C3	1.351(4)
Cl1−Al1−Cl2	113.48(6)	Cl3−Al1−S1	110.09(5)
C1−S1−Al1	98.79(9)	N1−C1−S1	125.7(2)
C3−C2−N1	106.9(2)	N2−C1−N1	107.4(2)

The N1−C1−N2 angle in the imidazole ring of **5** [104.8(3)°] lies between the corresponding angles of the free carbene 1,3,4,5-tetramethylimidazole-2-ylidene [101.3(2)° from X-ray, and 101.9(1)° and 102.0(1)° from neutron diffraction experiments on the perdeuterated compound][20] and that of an imidazolium salt [e.g. 108.6(4)° in **7**·THF]. These findings are in agreement with those of previously reported compounds.[1,2] For comparison, the N1−C1−N2 angle in **8** is 107.4(2)°.

In summary, we have prepared the first NHC adducts of an aluminum and a gallium trihalide, and report the first X-ray crystal structure of an aluminum halide carbene adduct. Moreover, an imidazolium tetrachloroaluminate and a thione adduct of $AlCl_3$ were also synthesized and structurally characterized.

Experimental Section

All manipulations were performed under a dry and oxygen-free atmosphere (N_2 or Ar) using Schlenk line and glove box techniques. Melting points are not corrected. X-ray single-crystal structure analyses were performed on a Stoe−Siemens four circle (**5**·$0.5C_7H_8$ and **8**) or a Stoe IPDS2 (**7**·THF) diffractometer with Mo-K_α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined with full-matrix least-squares on F^2 using SHELX-97.[21] Crystallographic data are summarized in Table 4. CCDC-234360 (**5**·$0.5C_7H_8$), -234361 (**7**·THF) and -234362 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Preparation of 5: Toluene (30 mL) was added at room temperature to a mixture of $AlCl_3$ (0.64 g, 4.80 mmol, 1.12 equiv.) and 1,3,4,5-tetramethylimidazole-2-ylidene[10] (0.55 g, 4.27 mmol, 1.0 equiv.). The mixture was stirred for 30 min, and the $AlCl_3$ dissolved. The mixture was filtered and concentrated in vacuo to 15 mL. A brown

Table 4. Crystallographic data

	5·$0.5C_7H_8$	**7**·THF	**8**
Formula	$C_{10.50}H_{16}AlCl_3N_2$	$C_{31}H_{45}AlCl_4N_2O$	$C_7H_{12}AlCl_3N_2S$
M	303.58	630.47	289.58
T	200(2) K	133(2) K	200(2) K
Crystal system	triclinic	triclinic	orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	$Pbca$
a (Å)	8.583(10)	9.937(3)	13.022(3)
b (Å)	8.903(10)	12.702(7)	13.368(4)
c (Å)	10.73(3)	14.265(5)	15.025(5)
α (°)	85.3(2)	82.85(3)	90
β (°)	79.20(6)	82.25(3)	90
γ (°)	68.57(7)	78.66(4)	90
V (nm^3)	0.75(1)	1.7404(12)	2.6155(12)
Z	2	2	8
$\delta_{calcd.}$ (Mg m^{-3})	1.344	1.203	1.471
μ (mm^{-1})	0.649	0.390	0.894
F(000)	314	668	1184
Crystal size (mm)	1.00 × 0.70 × 0.60	0.30 × 0.30 × 0.20	1.00 × 0.80 × 0.20
θ (°)	3.71−24.95	2.08−24.63	3.69−25.06
Index range	$-9 \le h \le 10$, $-10 \le k \le 10$, $-5 \le l \le 12$	$-11 \le h \le 11$, $-14 \le k \le 14$, $-16 \le l \le 16$	$-3 \le h \le 15$, $-15 \le k \le 15$, $-17 \le l \le 17$
Reflexes, collected/unique	3031/2600	32460/5821	3030/2295
R_{int}	0.0351	0.0948	0.0700
Completeness to θ (%)	99.0	99.0	99.5
Data/Restraints/Parameter	2600/265/170	5821/0/360	2295/0/132
Goodness-of-fit on F^2	1.103	1.010	1.049
R values [$I > 2\,\sigma(I)$]	$R_1 = 0.0726$, $wR_2 = 0.2270$	$R_1 = 0.0801$, $wR_2 = 0.1821$	$R_1 = 0.0540$, $wR_2 = 0.1348$
R values (all data)	$R_1 = 0.0757$, $wR_2 = 0.2314$	$R_1 = 0.1094$, $wR_2 = 0.1985$	$R_1 = 0.0584$, $wR_2 = 0.1411$
Largest diff. peak and hole [max and min] (e· Å^{-3})	1.483, −0.778	0.872, −0.408	0.737, −0.550

oily by-product was also formed and could be separated off during filtration. The solution was stored for two weeks at −25 °C to give colorless crystals of **5**. Colorless plates of **5**$\cdot$0.5C_7H_8 suitable for X-ray single-crystal structure analysis were obtained from a concentrated solution in toluene at 4 °C. The crystals were dried in vacuo. Yield 0.62 g (2.41 mmol, 56%). M.p. 130 °C. ^{1}H NMR (500 MHz, C_6D_6): δ = 1.15 (s, 6 H, NCH_3), 3.23 (s, 6 H, CCH_3) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ = 7.9 [C(4,5)CH_3], 34.0 (NCH_3), 125.6 [*C*(4,5)], 154 (very broad, carbene-*C*) ppm. ^{27}Al NMR (78.2 MHz, C_6D_6): δ = 103 ppm. MS (EI): *m*/*z* = 256 [M^+, 3], 221 (M^+ − Cl, 13), 124 ($C_7H_{12}N_2$, 100). IR (Nujol, KBr plates): ṽ = 1643, 1580, 1207, 1100, 1031, 487 cm^{-1}. $C_7H_{12}AlCl_3N_2\cdot C_{3.5}H_4$ (257.52): calcd. C 32.65, H 4.70, N 10.88; found C 33.11, H 4.65, N 10.67.

Preparation of 6: A solution of 1,3,4,5-tetramethylimidazole-2-ylidene (0.40 g, 3.23 mmol, 1.0 equiv.) in toluene (18 mL) was slowly added to cooled (−196 °C) $GaCl_3$ (0.57 g, 3.24 mmol, ca. 1.0 equiv.). The mixture was slowly warmed to room temperature while stirring, and stirring was continued for an additional 30 min at this temperature. The mixture was concentrated to about 12 mL, filtered, and stored at −25 °C to afford a colorless crystalline material of **6**$\cdot$0.70C_7H_8. Small amounts of a brown oily by-product formed during the reaction could be separated during filtration. Yield 0.73 g (2.00 mmol, 62%) of **6**$\cdot$0.70C_7H_8. M.p. approximately 110 °C. ^{1}H NMR (300 MHz, C_6D_6) [toluene resonances are not given]: δ = 1.05 (s, 6 H, NCH_3), 3.19 (s, 6 H, CCH_3) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ = 7.6 [C(4,5)CH_3], 33.8 (NCH_3), 125.6 [*C*(4,5)] ppm. MS (EI): *m*/*z* = 300 [M^+, 1], 265 (M^+ − Cl, 25), 124 ($C_7H_{12}N_2$, 100). IR (Nujol, KBr plates): ṽ = 1645, 1261, 1093, 1031, 848, 800, 570, 370 cm^{-1}. $C_7H_{12}Cl_3GaN_2\cdot C_{4.9}H_{5.6}$ (364.77): calcd. C 39.18, H 4.68, N 7.68; found C 38.98, H 4.65, N 7.50.

Preparation of 7: Toluene (50 mL) and THF (50 mL) were added to a mixture of $AlCl_3$ (0.56 g, 4.20 mmol, 1.1 equiv.) and 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene (1.47 g, 3.80 mmol, 1.0 equiv.). The mixture was stirred for 1 h and subsequently filtered. Yellow crystals of **7**$\cdot$THF were obtained at 2 °C. Yield 0.98 g (1.56 mmol, 41%). M.p. 260 °C: ^{1}H NMR (300 MHz, CD_3OD) [THF resonances are not given]: δ = 1.22 [d, *J* = 6.9 Hz, 12 H, CH(CH_3)$_2$], 1.34 [d, *J* = 6.9 Hz, 12 H, CH(CH_3)$_2$], 2.45 [sept, *J* = 6.9 Hz, 4 H, *CH*(CH_3)$_2$], 7.50 (d, *J* = 7.6 Hz, 4 H, *m*-ArH), 7.67 (t, *J* = 7.6 Hz, 2 H, *p*-ArH), 8.27 (d, *J* = 2.5 Hz, 2 H, C*H*), 9.97 (t, *J* = 2.5 Hz, 1 H, N_2C*H*) ppm. ^{13}C NMR (126 MHz, CD_3OD): δ = 23.9, 24.7, 30.4, 126.0, 127.6, 131.5, 133.4, 141.1, 146.5 ppm. MS (EI): *m*/*z* = 484 [$AlCl_2C_3N_2H(Dipp)_2^+$, 15], 451 [$AlClC_3N_2H(Dipp)_2^+$, 2], 389 [$C_3N_2H_3(Dipp)_2^+$, 100]. MS (FAB) cations: *m*/*z* = 389 [$C_3N_2H_3(Dipp)_2^+$, 100]. IR (Nujol, KBr plates): ṽ = 1643, 1600, 1540, 1331, 1206, 1062, 953, 804, 756, 683, 616, 491 cm^{-1}. $C_{27}H_{37}AlCl_4N_2\cdot C_4H_8O$ (630.49): calcd. C 59.05, H 7.19, N 4.44; found C 58.55, H 7.03, N 4.68.

Preparation of 8: Toluene (25 mL) was added to a mixture of $AlCl_3$ (0.50 g, 3.75 mmol, 1.0 equiv.) and 1,3,4,5-tetramethylimidazole-2(3*H*)-thione[10] (0.585 g, 3.75 mmol, 1.0 equiv.), stirred for 15 h at room temperature, 30 min at 50 °C, and finally filtered at this temperature. Storing the solution at 4 °C afforded crystals of **8**. Yield 0.63 g (2.18 mmol, 58%). M.p. approximately 165 °C (decomposed; in general decomposition at temperatures above about 100 °C). ^{1}H NMR (300 MHz, C_6D_6): δ = 1.27 (s, 6 H, NCH_3), 3.12 (s, 6 H, CCH_3) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ = 8.4, 31.5, 120.1, 161.6 ppm. MS (EI): *m*/*z* = 156 [{MeCCN(Me)}$_2$C=S, 100]. IR (Nujol, KBr plates): ṽ = 1639, 1262, 1100, 1020, 801, 612 cm^{-1}. $C_7H_{12}AlCl_3N_2S$ (289.59): calcd. C 29.03, H 4.18, N 9.67; found C 28.70, H 4.22, N 9.44.

Acknowledgments

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