Preparation of Geminal Donor-Acceptor Units by Reactions of Low Valent Metal Halides with Iminium Chlorides

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The organogallium compound $[\{Me_2NCH_2Ga(Cl,I)_2\}_2]$ (**1**) and the organoindium compounds $[Me_2NCH_2In(Cl,Br)_2]_2$ (**2**) and $[Me_2NCH_2InCl_2]_2$ (**3**) have been prepared by the reactions of the low valent metal halides "GaI", InBr and InCl with the iminium salt $[Me_2N=CH_2]Cl$. Compounds **1** and **2** are heterohalogen mixtures. These compounds were characterised by NMR spectroscopy and mass spectrometry, **1** furthermore by single crystal X-ray diffraction and **3** by elemental analysis. During the work-up procedure, minor amounts of hydrogen halide adducts of compounds **2** and **3** were isolated as single crystals, which contain a further equivalent of THF. These zwitter-ionic species $Me_2N(H)CH_2In(Br,Cl)_3\cdot THF$ (**2·H(Cl,Br)·THF**) and $Me_2N(H)CH_2InCl_3\cdot THF$ (**3·HCl·THF**) were identified by single crystal X-ray diffraction. Methylation reactions of compounds **1** and **2** with MeLi gave two well-established compounds $[\{Me_2NCH_2GaMe_2\}_2]$ and $[\{Me_2NCH_2InMe_2\}_2]$, which were obtained previously by different preparation procedures.

Key words: Iminium Salts, Geminal Systems, Metallated Amines, Gallium, Indium

Introduction

Organometallic compounds with donor functions in geminal position relative to the metal atom are a synthetically highly useful class of compounds [1]. Our research focuses on the synthesis of such earth metal compounds containing geminally linked donor and acceptor functions with the connectivity patterns M-C-N [2–9] and M-C-S [10] (M = Al, Ga, In). Such compounds are generally prepared from the corresponding α-lithiated heteroatom systems [11] by reactions with organometallic halides. As compared to phosphinomethyl (R_2PCH_2Li), oxymethyl $(ROCH_2Li)$ and thiomethyl lithium compounds $(RSCH_2Li)$, the aminomethyl lithium compounds (R_2NCH_2Li) are the most difficult to prepare, due to the fact that they are formally non-stabilised or even de-stabilised carbanionic compounds. Finding alternative synthetic pathways to MCN compounds avoiding the necessity of preparing the corresponding lithium alkyls is therefore highly desirable. In our earlier studies the insertion reactions of low valent metal halides $(GeCl_2, SnCl_2, "GaI"$ and InCl) into formamidinium chloride
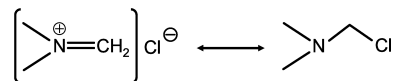
Scheme 1.

were tried [12]. Rather than giving the desired aminals metallated at the central carbon atom with a formula $(R_2N)_2CHMX_2$, the reactions afforded exclusively formamidinium salts of the anions $[GeCl_3]^-$, $[SnCl_3]^-$, $[Ga_2I_6]^{2-}$ and $[In_2Cl_6]^{2-}$.

N,N-Dimethylmethyleneiminium chloride is an ionic compound, which can be described as the ionic, mesomeric isomer of the hypothetical covalently bonded (chloromethyl)dimethylamine (Scheme 1).

The insertion reactions of low valent metal halide units could formally either occur into the covalent C-Cl bond or in an ionic mechanism with the iminium form of the reagent. The ionic mechanism involves the well established addition of chloride anions to $GeCl_2$ and $SnCl_2$, which leads to trichlorometallate(II) ions [13]. The resulting units MCl_3^- (M = Ge, Sn) can act as soft donor ligands, *e.g.* for late transition metals and gold(I) [14]. It is also known, that salts

of the $GeCl_3^-$ anion can be applied as nucleophilic reagents for the preparation of organometallic compounds $RGeCl_3$ [15]. Gallium(I) and indium(I) halides have also been used in insertion reactions into carbon-halogen bonds to form organogallium and -indium compounds [16,17].

It has been reported that the reaction of *N,N*-dimethylmethyleneiminium chloride, $[Me_2N=CH_2]Cl$, with $SnCl_2$ affords the ionic compound $[Me_2NCH_2]$ $[SnCl_3]$ [18] rather than the covalently bonded $Me_2NCH_2SnCl_3$. However, the silicon analogue $Me_2NCH_2SiCl_3$ was reported to be generated in the reaction of trichlorosilane with bis(dimethyl-amino)methane [18] (a reaction reported to lack re-producibility [19]) or – more straightforward – from iminium salts in Benkeser type reactions employ-ing the $HSiCl_3/NEt_3$ reagent [19]. Thus, the question arose, whether it would be possible to react $[Me_2N=CH_2]Cl$ with low valent group 13 metal halides to give compounds of the "covalent type" $Me_2NCH_2MCl_2$ (M = Ga, In). In this contribution, we report a new preparative pathway to species with geminal donor-acceptor units by the reactions of "GaI" and InCl with the iminium chloride $[Me_2N=CH_2]Cl$. The crys-tal structures of some of the products have been deter-mined and the alkylation reactions with methyllithium were studied.

Results and Discussion

Reaction of [Me₂N=CH₂]Cl with "GaI"

During the reaction of *N,N*-dimethylmethylene-iminium chloride with "gallium(I) iodide", prepared from elemental gallium and iodine [20] in THF, the di-agnostic colour of the low valent metal halide ("GaI": green) disappeared and the reaction mixture turned dark grey upon warming to ambient temperature. Heat-ing the grey filtration residue led to melting and the occurrence of a bright metal mirror on the walls of the glassware. This result indicated that elemental gallium was produced in a redox reaction.

Rather than generating the ionic species, the reactions of "GaI" led to the formation of a mix-ture of species described by the formula $[\{Me_2NC$ $H_2Ga(Cl,I)_2\}_2]$ (**1**) (Scheme 2), consisting of four products shown in Scheme 3 (M = Ga, X = I, X' = Cl) with covalent Ga-C-N units: one homohalogen compound $[Me_2NCH_2GaI_2]_2$ (Scheme 3a) and three heterohalogen compounds: $[(Me_2NCH_2GaClI)(Me_2NCH_2GaI_2)]$ (Scheme 3b),
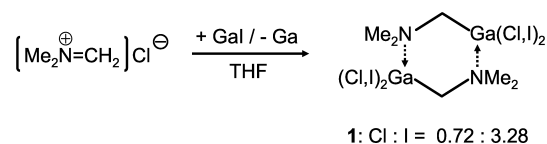
Scheme 2.
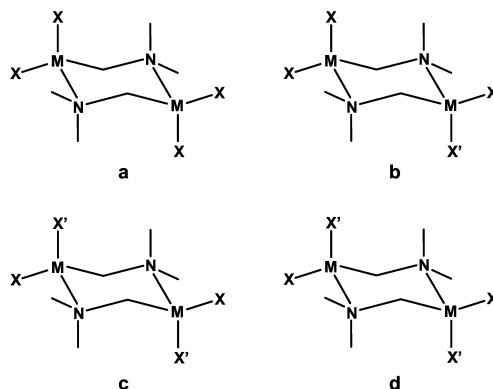
Scheme 3.

$[(Me_2NCH_2GaClI)_2]$ (Scheme 3c) and $[(Me_2NCH_2-GaCl_2)(Me_2NCH_2GaClI)]$ (Scheme 3d).

An important contribution to the identification of the mixed composition stems from the mass spectra of the isolated product (Fig. 1). There are four groups of mass peaks with highest intensities at $m/z = 636$ (80% rel. intensity), 545 (100% rel. intensity), 453 (36% rel. intensity) and 361 (5% rel. intensity) cor-responding to the cations $\{[Me_2NCH_2GaI_2]_2-I\}^+$, $\{[(Me_2NCH_2Ga)_2ClI_3]-I\}^+$, $\{[Me_2NCH_2GaICl]_2-I\}^+$ and $\{[(Me_2NCH_2Ga)_2ICl_3]-I\}^+$ generated from the four compounds listed in Scheme 3, respectively (corresponding to the isotopomers comprising ^{35}Cl and ^{69}Ga). It should be mentioned that there are no parent molecular mass peaks found for any of these compounds.

The mixed species could not be separated from one another. The mixture was obtained as a colourless, co-crystalline material upon cooling a THF solution to -25 °C. The presence of a mixture of at least four compounds leads to a complex ^1H NMR spectrum (d^8-THF). The chemical shifts stemming from the methyl protons at the nitrogen atoms fall into a small range from 2.7 to 3.1 ppm, which is within the established range for methyl groups bonded to N atoms [21]. The methylene protons give rise to a rather broad peak at 1.4 ppm. No further assignments have been made. Due to the low concentration of the NMR sample, the ^{13}C NMR signals could not be clearly detected.
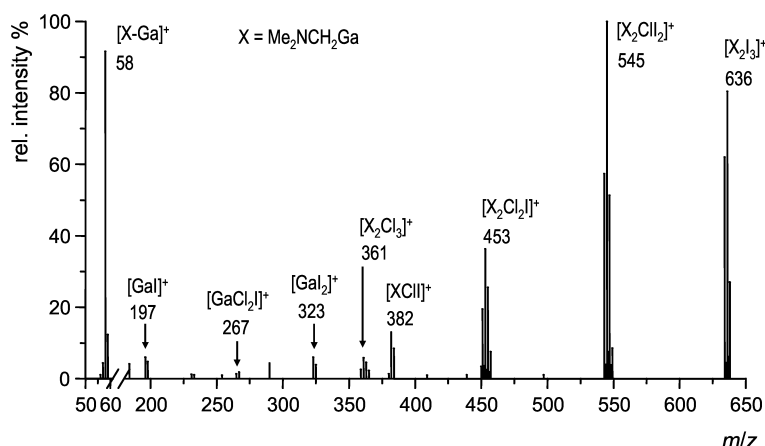
Fig. 1. Mass spectrum of the cocrystalline [{Me$_2$NCH$_2$Ga(I,Cl)$_2$}$_2$] (**1**) (X = Me$_2$NCH$_2$Ga).
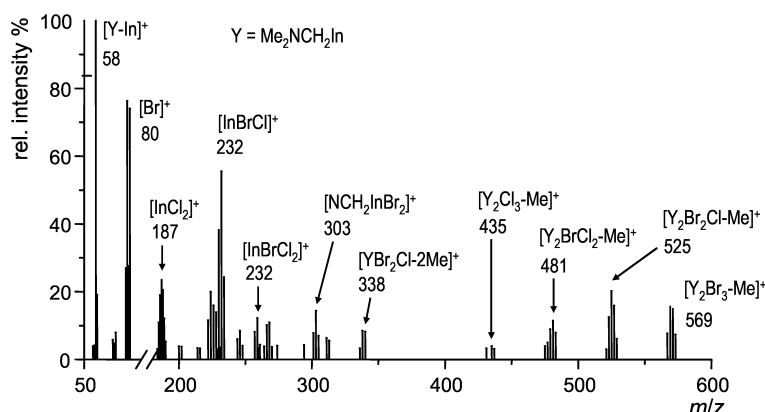
Fig. 2. Mass spectrum of Me$_2$NCH$_2$-In(Br,Cl)$_2$ (**2**) (Y = Me$_2$NCH$_2$In).

The crystal structure determination of the mixed halide is described below.

Reaction [Me$_2$N=CH$_2$]Cl with InBr

In the case of the reaction of the iminium salt [Me$_2$N=CH$_2$]Cl with InBr in THF, the vanishing of the diagnostic red colour of InBr and the formation of a metal mirror gave evidence for redox reactions.

A product of the composition Me$_2$NCH$_2$In(Cl,Br)$_2$ (**2**) was isolated by precipitation from the reaction mixture upon cooling. It was characterised by ^{1}H NMR spectroscopy and mass spectrometry. As compared with the ^{1}H NMR signals of the product **1**, the ^{1}H NMR spectrum of product **2** in d$_8$-THF solution has a much narrower range (3.0 – 3.1 ppm) for the methyl protons and a sharper peak (1.3 ppm) for the methylene protons. In the mass spectrum of product **2** (Fig. 2) the signals related to four homo- and hetero-halogen species (Scheme 3: M = In,

X = Br, X' = Cl), namely [(Me$_2$NCH$_2$InBr$_2$)$_2$], [(Me$_2$NCH$_2$InClBr)(Me$_2$NCH$_2$InBr$_2$)], [(Me$_2$NCH$_2$InBrCl)$_2$] and [(Me$_2$NCH$_2$InCl$_2$)(Me$_2$NCH$_2$InClBr)], were found at m/z = 569 (16% rel. intensity), 525 (20% rel. intensity), 481 (12% rel. intensity) and 435 (4% rel. intensity) corresponding to the {[Me$_2$NCH$_2$InBr$_2$]$_2$-Me-Br}$^+$, {[(Me$_2$NCH$_2$In)$_2$Br$_3$Cl]-Me-Br}$^+$, {[Me$_2$NCH$_2$InBrCl]$_2$-Me-Br}$^+$ and {[(Me$_2$NCH$_2$In)$_2$BrCl$_3$]-Me-Br}$^+$ cations, respectively (calculated for the isotopes ^{35}Cl and ^{69}Ga, Fig. 2). As for **1**, in no case the molecular mass peaks were detected.

From the precipitate generated by cooling the THF solution of the reaction mixture **2** some well formed crystals were isolated before drying of the bulk product in vacuum. They were examined by X-ray crystallography (see below) and are species, resulting from the addition of one equivalent of hydrogen halide (HCl, HBr) and saturation of the coordination sphere of the indium atom by one molecule of THF:

$$\left[Me_2\overset{\oplus}{N}=CH_2\right]Cl^{\ominus}$$

InBr
THF

Me_2N ⌢ $In(Br,Cl)_2$

2

HCl/HBr
THF
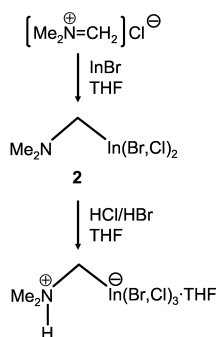
$Me_2\overset{\oplus}{N}$ ⌢ $\overset{\ominus}{In}(Br,Cl)_3$·THF
|
H

2·H(Cl,Br)·THF: Br:Cl = 1.75:1.25

Scheme 4

$$\left[Me_2\overset{\oplus}{N}=CH_2\right]Cl^{\ominus}$$

InCl | THF

Me_2N ⌢ $InCl_2$

3

HCl | THF

$Me_2\overset{\oplus}{N}$ ⌢ $\overset{\ominus}{In}Cl_3$·THF
|
H

3·HCl·THF

Scheme 5

$Me_2N(H)CH_2In(Br,Cl)_3$·THF (**2·H(Cl,Br)·THF**). The overall formation of this product is shown in Scheme 4. The origin of the equivalent of HCl or HBr remains unclear and could possibly stem from a partial hydrolysis of the product.

Such zwitterionic adducts of one equivalent of hydrogen halide to an aminomethyl-element compound are known from the respective silicon compounds – the aminomethylsilanes – which are a class of compounds intensively investigated by R. Tacke and coworkers [22]. The existence of **2·H(Cl,Br)·THF** shows, that the In-C bond withstands the presence of acids even if present as ammonium ion in closest proximity.

From the missing NMR peaks of nitrogen bonded protons or those belonging to THF units and the mass spectrum of the isolated dried product **2**, it can be concluded that the solvating THF molecules and the equivalent of hydrogen halide were absent in the bulk product. Due to the fact that the indium atoms cannot saturate their coordination spheres in the monomeric $Me_2NCH_2In(Br,Cl)_2$ molecules (**2**), these units of **2** dimerise as is indicated by the masses found in the mass spectrum described above. Compound **2** is therefore very likely to adopt the structure of a six-membered ring dimer as was found for **1** (see the crystal structure description below).

Reaction of [Me₂N=CH₂]Cl with InCl

When InCl was applied as the insertion reagent instead of InBr, chlorine was the only sort of halogen present in the reaction mixture. A similar THF solvated zwitter-ionic organoindium compound $Me_2N(H)CH_2InCl_3$·THF (**3·HCl·THF**) precipitated in small amounts as colourless crystals from the THF solution of the reaction mixture and was characterised by crystal structure determination (see below). Again, the origin of the equivalent of HCl remains unclear.
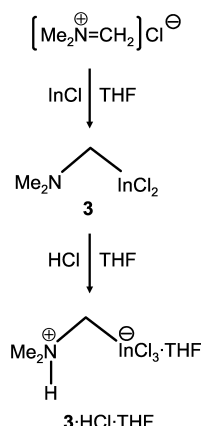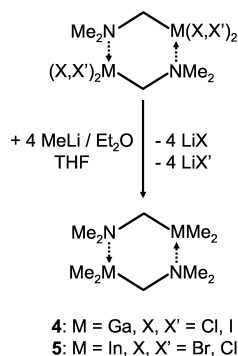
However, isolation of the bulk product by precipitation from the solution of the reaction mixture in the cold, flitration and subsequent drying *in vacuo* led to the isolation of **3** (Scheme 5), the HCl and THF free pendant to **3·HCl·THF**. This compound was identified by NMR spectroscopy in CD_3CN solution and by elemental analysis. In the NMR spectrum, there are no peaks corresponding to the chemical shifts of solvating THF molecules and to nitrogen-bound protons. This leads to the same conclusion as in the case of **2** that there are no solvating THF and "extra" HCl equivalents in the main product. The elemental analysis data are also consistent with this composition.

Reactions of [{Me₂NCH₂Ga(I,Cl)₂}₂] and [{Me₂NCH₂In(Br,Cl)₂}₂] with MeLi

The reactions of [{$Me_2NCH_2Ga(I,Cl)_2$}₂] and [{$Me_2NCH_2In(Br,Cl)_2$}₂] with MeLi solutions in Et_2O were carried out in THF at −78 °C. The methylated products are the well-documented organometallic compounds, [($Me_2NCH_2GaMe_2$)₂] (**4**) [2] and [($Me_2NCH_2InMe_2$)₂] (**5**) [8], containing geminal M-C-N (M = Ga, In) units (Scheme 6). They were ear-

Me_2N ⌢ $M(X,X')_2$
$(X,X')_2M$ ⌢ NMe_2

+ 4 MeLi / Et_2O - 4 LiX
THF   - 4 LiX'

Me_2N ⌢ MMe_2
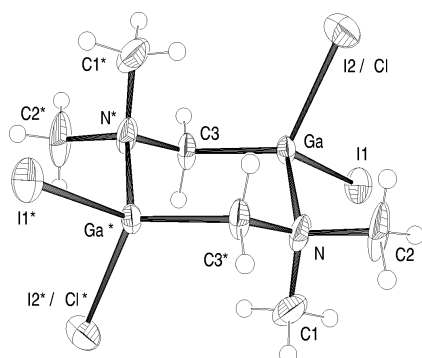Me_2M ⌢ NMe_2

4: M = Ga, X, X' = Cl, I
5: M = In, X, X' = Br, Cl

Scheme 6

Fig. 3. Crystal structure of $[\{Me_2NCH_2Ga(I,Cl)_2\}_2]$ (**1**) (the position of I1 is fully occupied by iodine, the ratio I2:Cl refined to 0.64:0.36). ORTEP drawing with 50% probability ellipsoids (symmetry transformations used to generate equivalent atoms: $x+1, -y+2, -z+2$).

lier obtained from the reactions of $LiCH_2NMe_2$ with Me_2GaCl or Me_2InCl, respectively.

Compounds **4** and **5** were characterised by ^1H and ^{13}C NMR spectroscopy; all the data compare well to those from the earlier studies [2, 8].

Crystal structure of $[\{Me_2NCH_2Ga(I,Cl)_2\}_2]$

Similar to $[(Me_2GaCH_2NMe_2)_2]$ [2] with the methyl groups at Ga atoms, $[\{Me_2NCH_2Ga(I,Cl)_2\}_2]$ (**1**) crystallizes also in the triclinic space group $P\bar{1}$ and has a chair conformation with a centre of symmetry in the middle of the six-membered $Ga_2C_2N_2$ ring (Fig. 3).

The refinement of a suitable model using the X-ray scattering intensities obtained from a single crystal showed the presence of a cocrystallisate of only three components (Scheme 3: a, b and c; M = Ga, X = I, X' = Cl) with a refined empirical molecular formula $C_6H_{16}Cl_{0.72}Ga_2I_{3.28}$. The relative intensity values from the mass spectra confirm this crystallographically refined ratio. The equatorial positions at the Ga atoms are occupied exclusively by iodine atoms, while the axial positions are occupied by the chlorine and iodine atoms in a ratio of Cl:I = 0.36:0.64.

The bond lengths and angles (Table 1) in the six-membered $N_2C_2Ga_2$ ring of **1** are quite similar to the corresponding values in $[Me_2GaCH_2NMe_2]_2$ [2]. The bond length Ga-N [2.025(5) Å] in the cocrystallisate represents of course an arrange value for the different components of the crystals (as do all the other structural parameters) and is slightly shorter than that [2.093(2) Å] in $[(Me_2GaCH_2NMe_2)_2]$ [2]. The N-C-Ga angles in **1** [119.1(4)°] and in $[(Me_2GaCH_2NMe_2)_2]$ [119.7(2)°] [2] are compa-

Table 1. Selected bond lengths and angles of $[\{Me_2NCH_2Ga(I,Cl)_2\}_2]$ (**1**) [Å, °] (symmetry transformations used to generate equivalent atoms denoted by an asterisk: $x+1, -y+2, -z+2$).

Distances		Angles	
I1-Ga	2.496(1)	C3-Ga-I2	120.6(2)
I2-Ga	2.469(2)	N-Ga-I2	102.8(2)
Cl-Ga	2.136(13)	C3-Ga-I1	110.8(2)
Ga-C3	1.980(6)	N-Ga-I1	107.0(2)
Ga-N	2.025(5)	Cl-Ga-I1	107.3(5)
N-C1	1.483(11)	I2-Ga-I1	107.1(4)
N-C2	1.485(9)	C1-N-C2	108.3(7)
N-C3*	1.490(9)	C1-N-C3*	110.6(6)
C3-N*	1.490(9)	C2-N-C3*	109.4(6)
		C1-N-Ga	109.6(5)
		C2-N-Ga	112.5(5)
		C3*-N-Ga	106.4(4)
		C3-Ga-N	107.6(3)
		C3-Ga-Cl	117.3(6)
		N-Ga-Cl	106.4(6)
		N*-C3-Ga	119.1(4)

rable, but both are, as expected, distinctly larger than the ideal tetrahedral angle.

Crystal structures of $Me_2N(H)CH_2In(Br,Cl)_3·THF$ and $Me_2N(H)CH_2InCl_3·THF$

$Me_2N(H)CH_2In(Br,Cl)_3·THF$ and $Me_2N(H)CH_2In$ $Cl_3·THF$ crystallize both in the monoclinic space group $P2_1/c$ (Figs. 4 and 5).

The refinement of a suitable model of $Me_2N(H)$ $CH_2In(Br,Cl)_3·THF$ using the X-ray scattering intensities obtained from a single crystal gives a cocrystallisate with an empirical molecular formula $C_7H_{17}Br_{1.75}Cl_{1.25}InNO$. The three halogen atom sites at the In atom were refined in split positions whereby the atom Cl1 in axial position of the trigonal pyramidal coordination sphere of indium had an occupancy of 0.75, while the split position Br1 had an occupancy
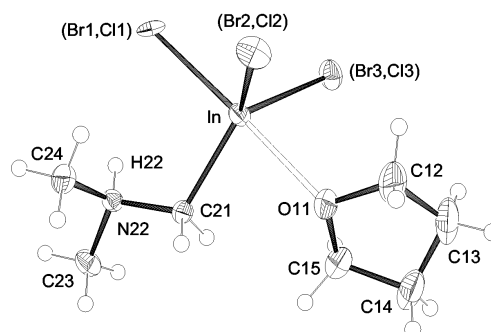

Fig. 4. Crystal structure of $Me_2N(H)CH_2In(Br,Cl)_3·THF$ [**2**·H(Cl,Br)·THF] (Br:Cl = 1.75:1.25). ORTEP drawing with 50% probability ellipsoids.

Table 2. Selected bond lengths and angles of Me$_2$N(H) CH$_2$In(Br,Cl)$_3$·THF [**2**·H(Cl,Br)·THF] [Å, °].The positions of Cl1, Br2 and Br3 are occupied by 75% of the given halogen atom and by 25% of the alternative and were refined in split positions (see text). The table entries refer to the most abundant species.

Distances		Angles	
In-C21	2.173(2)	Cl1-In-C21	96.3(2)
In-Cl1	2.578(6)	Cl1-In-O11	177.1(2)
In-O11	2.447(2)	Br2-In-Cl1	97.5(2)
In-Br2	2.487(3)	Br3-In-Cl1	95.9(2)
In-Br3	2.540(2)	Br2-In-Br3	109.5(9)
N22-C21	1.500(3)	C21-In-Br2	123.3(1)
N22-C24	1.485(4)	C21-In-Br3	123.3(1)
N22-C23	1.491(3)	O11-In-Br2	85.2(1)
N22-H22	0.87 (3)	O11-In-Br3	84.3(1)
		C22-In-O11	81.3(1)
		N22-C21-In	115.2(1)
		C24-N22-C23	110.6(2)
		C24-N22-C21	111.7(2)
		C23-N22-C21	111.3(2)
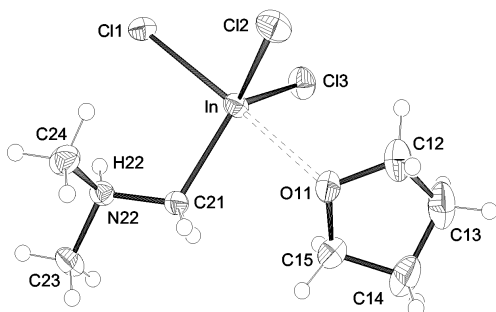
Fig. 5. Crystal structure of Me$_2$N(H)CH$_2$InCl$_3$·THF (**3**·HCl·THF), ORTEP drawing with 50% probability ellipsoids.

of 0.25. The equatorial positions (Br2 and Br3) were found to be preferably occupied by bromine, both with occupancies of 0.75, leading to corresponding occupancy factors for the chlorine split positions of 0.25. The overall ratio of Br:Cl is thus 1.75:1.25.

As both crystal structures and coordination geometries in Me$_2$N(H)CH$_2$In(Br,Cl)$_3$·THF (Table 2) and Me$_2$N(H)CH$_2$InCl$_3$·THF (Table 3) are quite similar, only the structure of **3**·HCl·THF which does not suffer from averaging the structural parameters resulting from the presence of more than one species, is discussed here.

The In-C-N angle of the protonated monomeric molecule in the structure of **3**·HCl·THF, unlike the N-C-In angle in [Me$_2$InCH$_2$NMe$_2$]$_2$ [119.7(1)°] [8] which is subject to ring-strain, has a smaller value [115.2(1)°] (Table 3), but is still more than 5° larger than the ideal tetrahedral angle. In contrast to the

Table 3. Selected bond lengths and angles of Me$_2$N(H) CH$_2$InCl$_3$·THF (**3**) [Å, °].

Distances		Angles	
In-C21	2.173(2)	Cl2-In-Cl3	108.6(1)
In-Cl2	2.377(1)	C21-In-O11	81.8(1)
In-Cl3	2.392(1)	Cl2-In-O11	85.7(1)
In-O11	2.429(2)	Cl3-In-O11	84.8(1)
In-Cl1	2.520(1)	C21-In-Cl1	96.3(1)
N22-C24	1.481(3)	Cl2-In-Cl1	96.8(1)
N22-C23	1.493(3)	Cl3-In-Cl1	95.0(1)
N22-C21	1.495(3)	O11-In-Cl1	177.5(1)
N22-H22	0.87 (2)	C24-N22-C23	110.2(2)
		C24-N22-C21	112.2(2)
		C23-N22-C21	111.2(2)
		C21-In-Cl2	124.7(1)
		C21-In-Cl3	123.4(1)
		N22-C21-In	115.2(1)

four-coordinate In atom in [Me$_2$InCH$_2$NMe$_2$]$_2$ [8], the In atom in **3**·HCl·THF is five-coordinate. The sum of the three angles (C21-In-Cl2, C21-In-Cl3, Cl2-In-Cl3) at the In atom is 356.7°, thus the In atom is located approximately in the plane spanned by the atoms of C21, Cl2 and Cl3. The O atom of the THF molecule and the Cl1 atom are bonded to the central In atom from two sides of this triangle and the three atoms (Cl1, In, O) are almost linear with the atoms defining an angle of 177.5(1)°. The coordination geometry of the In atom is thus trigonal pyramidal. Consistently, the length of the axial Cl1-In bond [2.520(1) Å] is much longer than the Cl-In bonds in the equatorial positions [In-Cl2 2.377(1) Å, In-Cl3 2.392(1) Å].

Conclusion

In contrast to the ionic compound [Me$_2$N= CH$_2$]SnCl$_3$, formed in the reaction of the iminium chloride [Me$_2$N=CH$_2$]Cl with tin(II) chloride, the reaction of this iminium chloride with gallium(I) and indium(I) halides leads to the formation of α-metallated trimethylamine derivatives with distinct metal-carbon bonds. This reaction is thus a new synthetic route to amines α-metallated by group 13 elements. It seems surprising that the elements gallium and indium behave in this respect more similar to the semimetal silicon (Me$_2$NCH$_2$SiCl$_3$ has a covalent C-Si bond) than to the metal tin. On the other hand it is also worth noting that in contrast to the iminium chloride [Me$_2$N=CH$_2$]Cl, formamidinium chloride [(Me$_2$N)$_2$CH]Cl does not form metal carbon bonds upon reaction with low valent halides of gallium and indium, but rather leads to disproportionation of the metal compounds.

It would be interesting to try whether the preparative pathway to α-metallated amines by reactions of

iminium halides with low valent metal halides can also be applied to the chemistry of aluminium. Future work could therefore include reactions with donor stabilised Al(I) bromide [23] or Al(I) iodide [24], which are very reactive, and only accessible with specialised equipment as was shown in the past by the impressive work of H. Schnöckel and his collaborators.

Experimental Section

General remarks: All reactions and manipulations were carried out under a dry nitrogen atmosphere with Schlenk and high vacuum techniques using standard double manifolds or a glove box operated under argon. Solvents were purified and dried by standard techniques immediately prior to use. All NMR data were collected on a Bruker AM 200 (operating at 200 MHz for ^{1}H and 75 MHz for ^{13}C) FT NMR spectrometer. Chemical shifts are quoted relative to TMS. A Bruker Apex X-ray diffractometer (for **1**) and a Nonius Kappa-CCD X-ray diffractometer (for **2** and **3**) were used to collect the scattering intensities for the single crystal structure determinations (both $\lambda = 0.71073$ Å).

[{Me$_2$NCH$_2$Ga(Cl,I)$_2$}$_2$] (**1**): GaI [20] (1.0 g, 5.0 mmol) was added to a stirred solution of [Me$_2$N=CH$_2$]Cl (0.46 g, 5.0 mmol) in 50 ml THF with the aid of a solid transfer container at -25 °C. This salt addition was performed in small portions in order to minimise temperature fluctuations. The reaction mixture was stirred for 4 h at this temperature and allowed to warm up to ambient temperature overnight. The mixture was filtered through a cannula equipped with a glass wool filter and a clear solution was obtained. The clear filtrate was concentrated under vacuum. The vessel with the solution was immersed into a 1 l Dewar container filled with ethanol and was then allowed to cool slowly to -25 °C. Well formed crystals were obtained in this way. Yield 0.27 g.

^{1}H NMR (d$_8$-THF): $\delta = 2.74 - 3.13$ (NCH$_3$), 1.4 (GaCH$_2$N). – MS [EI, 70 eV] m/z(%) = 636 (80) [(C$_6$H$_{16}$Ga$_2$I$_3$N$_2$)$^+$], 545 (100) [(C$_6$H$_{16}$ClGa$_2$I$_2$N$_2$)$^+$], 453 (36) [(C$_6$H$_{16}$Cl$_2$Ga$_2$IN$_2$)$^+$], 382 (13) [(C$_3$H$_8$GaI$_2$N)$^+$], 361 (5) [(C$_6$H$_{16}$Ga$_2$Cl$_3$N$_2$)$^+$], 323 (6) [(GaI$_2$)$^+$], 267 (2) [(GaCl$_2$I)$^+$], 196 (6) [(GaI)$^+$], 58 (91) [(Me$_2$NCH$_2$)$^+$].

Me$_2$NCH$_2$In(Br,Cl)$_2$·THF (**2**): The same procedure as for **1** was applied. InBr (1.01 g, 5.1 mmol), [Me$_2$N= CH$_2$]Cl (0.23 g, 2.5 mmol).

The product is a mixture with the empirical molecular formula [{Me$_2$NCH$_2$In(Br,Cl)$_2$}$_2$]. Yield 0.31 g. – ^{1}H NMR (d$_8$-THF): $\delta = 3.0 - 3.1$ (NCH$_3$), 1.3 (InCH$_2$N). – MS [EI, 70 eV] m/z (%) = 569 (16) [(C$_5$H$_{13}$In$_2$Br$_3$N$_2$)$^+$], 525 (20) [(C$_5$H$_{13}$ ClIn$_2$Br$_2$N$_2$)$^+$], 481 (12) [(C$_5$H$_{13}$Cl$_2$In$_2$BrN$_2$)$^+$], 435 (4) [(C$_5$H$_{13}$In$_2$Cl$_3$N$_2$)$^+$], 338 (8) [(NCH$_2$InBr$_2$Cl)$^+$], 303 (14) [(NCH$_2$ InBr$_2$)$^+$], 268 (10) [(InBrCl$_2$)$^+$], 232 (55) [(InBrCl)$^+$], 187 (23)

[(InCl$_2$)$^+$], 116 (30) [In$^+$], 80 (76) [Br$^+$], 58 (100) [(Me$_2$NCH$_2$)$^+$].

The few crystals obtained from the reaction mixture in THF solution upon cooling were used for structure determination by single crystal X-ray diffraction. These crystals contained Me$_2$N(H)CH$_2$In (Br,Cl)$_3$·THF, *i. e.* an adduct of HCl/HBr and THF to **2**.

Me$_2$NCH$_2$InCl$_2$ (**3**): The same procedure as for **1** was applied. InCl (0.75 g, 11.1 mmol), [Me$_2$N=CH$_2$]Cl (0.46 g, 5.0 mmol). Yield 0.39 g, 39%, m. p. 173 °C. – ^{1}H NMR (CD$_3$CN): $\delta = 2.92$ (s, 6H, NCH$_3$), 2.85 (s, 2H, InCH$_2$N). – ^{13}C NMR (CD$_3$CN): $\delta = 62.3$ (NC), 48.2 (InC). – C$_3$H$_8$Cl$_2$InN (243.8) calcd. C 14.78, H 3.31, N 5.74; found C 14.65, H 3.29, N 5.69.

The crystals obtained from the reaction mixture in THF solution upon cooling were used for structure determination by single crystal X-ray diffraction. These crystals contained Me$_2$N(H)CH$_2$InCl$_3$·THF, *i. e.* an adduct of HCl and THF to **2**.

[Me$_2$NCH$_2$GaMe$_2$]$_2$ (**4**): A solution of MeLi (2.0 ml, 1.6 M solution in Et$_2$O) was added dropwise to a solution of [(Me$_2$NCH$_2$Ga)$_2$ClI$_3$)] (assumed to be pure [(Me$_2$NCH$_2$Ga)$_2$ClI$_3$]), 0.54 g, 0.8 mmol) in 30 ml THF (25 ml) at -78 °C with vigorous stirring. The fact that the ratio I:Cl in **1** turned out to be 3.28:0.72 in [{Me$_2$NCH$_2$Ga(Cl,I)$_2$}$_2$] means that MeLi in this reaction is present in a small excess. The reaction mixture was stirred overnight at this temperature and then allowed to warm to ambient temperature. The mixture was filtered through a sintered glass filter (porosity no. 4) and the resulting clear solution was concentrated under vacuum until it became slightly cloudy. The vessel containing this solution was kept at -25 °C overnight. The crude product was isolated as a crystalline material by removing the clear supernatant liquid by a cannula equipped with a glass wool filter, and was further purified by sublimation at 45 °C (0.01 Torr). The spectroscopic data are consistent with those reported earlier [2]. Yield 0.13 g, 52% (based on the assumption of pure [(Me$_2$NCH$_2$Ga)$_2$ClI$_3$]).

[Me$_2$NCH$_2$InMe$_2$]$_2$ (**5**): The [{Me$_2$NCH$_2$In(Br, Cl)$_2$}$_2$] mixture was assumed to be pure [(Me$_2$NCH$_2$In Cl$_2$)$_2$] and four equivalents of MeLi solution in Et$_2$O were applied following the same procedure as for **4**.

MeLi (2.0 ml, 1.6 M solution in Et$_2$O), [(Me$_2$ NCH$_2$InCl$_2$)$_2$] (0.39 g, 0.8 mmol), sublimation temperature of [Me$_2$NCH$_2$InMe$_2$]$_2$: 55 °C (0.01 Torr). The spectroscopic data are consistent with those reported earlier [8]. Yield 1.4 g, 43% (based on the assumption of pure [(Me$_2$NCH$_2$InCl$_2$)$_2$]).

Crystal structure analyses. Single crystals of compounds **1**, **2**·H(Cl,Br)·THF and **3**·HCl·THF were mounted under inert perfluoropolyether at the tip of a glass fiber and were cooled in the cryostream of the diffractometer. Structure solutions were carried out using direct methods, and the

Compound	[{Me$_2$NCH$_2$Ga(Cl,I)$_2$}$_2$] **1***	Me$_2$N(H)CH$_2$In(Br,Cl)$_3$·THF **2**·H(Cl,Br)·THF*	Me$_2$N(H)CH$_2$InCl$_3$·THF **3**·HCl·THF
Formula	C$_6$H$_{16}$Cl$_{0.72}$Ga$_2$I$_{3.28}$	C$_7$H$_{17}$Br$_{1.75}$Cl$_{1.25}$InNO	C$_7$H$_{17}$Cl$_3$InNO
Cryst. system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
Diffractometer	Bruker Apex	Nonius Kappa-CCD	Nonius Kappa-CCD
λ [Å]	0.71073	0.71073	0.71073
a [Å]	7.123(2)	10.473(1)	10.486(1)
b [Å]	7.636(2)	10.398(1)	10.153(1)
c [Å]	8.996(2)	12.927(1)	12.745(1)
α [°]	70.27(3)	90	90
β [°]	69.93(3)	107.43(1)	107.82(1)
γ [°]	64.92(3)	90	90
V [Å^3]	405.46(13)	1343.1(2)	1291.8(2)
ρ_{calc} [g cm^{-3}]	2.86	2.13	1.81
Z	1	4	4
μ [mm^{-1}]	9.7	7.2	2.4
T [K]	153(2)	198(2)	198(2)
$2\theta_{max}$ [°]	60.02	56.54	55.82
Measd. refl.	4607	9040	11423
Unique refl.	2311	3290	3056
Observed refl.	1898	3039	2767
R_{int}	0.033	0.039	0.048
Parameters	75	148	125
$R[I > 2\sigma(I)]$	0.046	0.024	0.025
wR^2 (all data)	0.119	0.057	0.063
ρ_{fin} (min/max) [eÅ^3]	$-1.192/2.151$	$-1.018/0.564$	$-0.873/0.660$
CCDC No.	292415	292417	292416

Table 4. Crystal and refinement data for compounds **1**, **2**·H(Cl,Br)·THF and **3**·HCl·THF.

* Cocrystalline compounds.

refinements of the structures were undertaken with the program SHELXTL 5.01 [25] for **1** and SHELXTL 6.10 [26] for compounds **2**·H(Cl,Br)·THF and **3**·HCl·THF. Non-hydrogen atoms were refined with anisotropic displacement parameters, hydrogen atoms isotropically with a riding model. Further details of data collection and refinement are listed in Table 4. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, Uk [fax: (+44)1223-336-033; email: deposit@ccdc.cam.ac.uk].

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