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# Reactions of trichlorogermane HGeCl<sub>3</sub> and dichlorogallane HGaCl<sub>2</sub> with pyridine donors

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The weak base pyridine has been found to deprotonate trichlorogermane HGeCl<sub>3</sub> with quantitative formation of pyridinium trichlorogermanate(II), Py-H<sup>+</sup>GeCl<sub>3</sub><sup>-</sup>, the pyramidal structure of the anion resembling that of the isoelectronic AsCl<sub>3</sub> molecule. This course of the reaction supports the assignment of an inverse polarization (-)Ge-H(+) of the bond in HGeCl<sub>3</sub> as compared to the (+)Si-H(-) bond in trichlorosilane HSiCl<sub>3</sub>, which is known to form a 1 : 2 adduct with pyridine instead. Germanium tetrachloride also undergoes simple addition reactions with pyridine leading ultimately *e.g.* to GeCl<sub>4</sub>L<sub>2</sub> with L = 4-ethyl-pyridine. Dichlorogallane gives 1 : 1 addition compounds (HGaCl<sub>2</sub>L) with L = pyridine, 4-dimethylamino-pyridine, 4-cyano-pyridine, and 3,5-dimethyl-pyridine, the molecular structures of which have been determined by single crystal X-ray diffraction. Simple tetrahedral arrays of substituents around the gallium center with only minor distortions, and characteristic Ga–H stretching vibrations in the IR spectra, show that the Ga–H bond is untouched in the addition reactions. The addition of two equivalents of 3,5-dimethyl-pyridine to HGaCl<sub>2</sub> affords the 1 : 2 complex which was shown to have a trigonal-bipyramidal geometry with the hydride ligand in an equatorial position. In order to provide benchmark data, the 1 : 1 adducts GaCl<sub>3</sub>(L) and GaH<sub>3</sub>(L) with L = 3,5-dimethyl-pyridine were also prepared and structurally characterized. Pyridinium tetrachlorogallate(III) takes up pyridine, but the extra ligand is attached to the cation *via* hydrogen bonding leaving the anion unchanged: [Py-H  $\cdots$  Py]<sup>+</sup>[GaCl<sub>4</sub>]<sup>-</sup>.

# Introduction

Owing to a discontinuity of many properties of the elements in Group IV, and of their electronegativity in particular,<sup>1</sup> the hydridic character of germanium hydrides is greatly reduced as compared to silicon hydrides. Thus germane GeH<sub>4</sub> is stable to water and even to acid, and chlorogermanes  $H_nGeCl_{4-n}$  may already be described as weak acids. Mechanistically, this acidic behaviour can be ascribed to the excellent leaving group properties of the corresponding anions, vic.  $[GeH_3]^-$  and  $[GeCl_3]^-$ , respectively.<sup>2</sup> It should be noted that this ionization out of an inverted polarization [from (+)Ge-H(-) to (-)Ge-H(+)] can be considered a redox reaction in that the germanium atoms change their formal oxidation state from +4 to +2, the two anions being hydride or chloride adducts of the germylenes GeH<sub>2</sub> or GeCl<sub>2</sub>, respectively. While this mode of reaction has been established with HGeCl<sub>3</sub> and strong bases like trimethylamine.<sup>3</sup> the course of reactions with weak bases like pyridine has not yet been followed. By contrast chlorosilanes  $H_nSiCl_{4-n}$  are known to form 1 : 1 and 1 : 2 adducts with tertiary amines<sup>4</sup> and pyridines<sup>5</sup> which is fully in agreement with the presence of (+)Si-H(-) bonds.

By contrast, such a discontinuity is not very pronounced in the series of the Group III elements,<sup>1</sup> and the hydridic character typical for aluminium hydrides is largely preserved in the gallium hydrides.<sup>6</sup> Gallium hydrides  $GaH_nCl_{3-n}$  and their adducts  $GaH_nCl_{3-n}(L)$  with donor ligands L show no protic character.

In the present study the different modes of reaction of trichlorogermane,<sup>2</sup> HGeCl<sub>3</sub>, and dichlorogallane,<sup>7</sup> HGaCl<sub>2</sub>, with pyridines have been investigated in order to probe the donor and acceptor properties towards ligands which are weak Brønsted bases, but strong nucleophiles for main group metals. Because there is still a paucity of structural data for gallium hydrides<sup>6,8,9</sup> and especially for complexes of dichlorogallane,<sup>9</sup> the crystal structures of a series of representative adducts with gallium in different coordination geometries have been determined.

## **Results and discussion**

#### **Preparative studies**

**Trichlorogermane HGeCl<sub>3</sub>.** Trichlorogermane HGeCl<sub>3</sub> is not a stable compound at room temperature, hydrogen chloride being slowly evolved with formation of GeCl<sub>2</sub> and its oligomers or adducts.<sup>2</sup> The substrate therefore has to be freshly prepared prior to reactions with donor molecules and preferably handled at low temperature. It can be dissolved in an excess of dry pyridine (Py) at -40 °C to give a clear solution. Evaporation of the solvent in a vacuum leaves a colourless crystalline residue, which can be crystallized from toluene, mp 114 °C, in quantitative yield calculated for a 1 : 1 adduct. This composition was confirmed by elemental analysis. The product is hygrocopic and decomposes in air. It can be dissolved in acetonitrile where it shows the <sup>1</sup>H and <sup>13</sup>C resonances typical for pyridinium salts. There is no absorption in the infrared spectrum which could be assigned to a Ge–H stretching vibration.

This result suggests that even the weak pyridine base deprotonates HGeCl<sub>3</sub> instead of forming an adduct HGeCl<sub>3</sub>(Py)<sub>n</sub> with the germanium atom featuring a higher coordination number. The crystal structure analysis (below) gave the final proof that the reaction afforded pyridinium trichlorgermanate(II), [Py-H]<sup>+</sup>[GeCl<sub>3</sub>]<sup>-</sup> (eqn. (1)).

$$HGeCl_3 + Py \longrightarrow [Py-H]^+[GeCl_3]^-$$
(1)

It should be noted that  $\text{GeCl}_4$  readily forms a stable 1 : 2 adduct with pyridine,  $\text{GeCl}_4(\text{Py})_2$ , which is known to have a *trans* structure.<sup>10</sup> To show that this is a general reaction, a 1 : 2 adduct of  $\text{GeCl}_4$  with 4-ethyl-pyridine was successfully prepared in the present study. It is obvious therefore that there is no steric hindrance or other kinetic effect to be expected for an addition of pyridine to  $\text{HGeCl}_3$  to give hypothetical adducts  $\text{HGeCl}_3(L)$  or even  $\text{HGeCl}_3(L)_2$ . Deprotonation and formation of pyridinium trichlorogermanites(II) is clearly the thermodynamically controlled process.

**Dichlorogallane HGaCl<sub>2</sub>.** Dichlorogallane HGaCl<sub>2</sub> forms a stable 1 : 1 adduct with pyridine, the IR spectrum of which shows a strong absorption for a Ga–H stretching vibration. Similar results were observed with 4-dimethylamino- and 4-cyano-pyridine, as well as with 3,5-dimethyl-pyridine. The results show that changes of the basic/nucleophilic character of the pyridine induced by different substituents in the *para*position, or a steric effect of *meta*-substituents, do not alter the course of the reaction (eqn. (2)).

$$(HGaCl_2)_2 + 2 Py \rightarrow 2 HGaCl_2(Py)$$
(2)

The molecular structures of all four complexes have been determined (below). For comparison of the structural data for the 3,5-dimethyl-pyridine complex, the corresponding compounds of gallane,  $H_3Ga(3,5-Me_2C_5H_3N)$ , and of gallium trichloride,  $Cl_3Ga(3,5-Me_2C_5H_3N)$ , were also synthesized and their structures determined. For the preparation of the GaH<sub>3</sub>-complex the reagents employed were LiGaH<sub>4</sub> and [3,5-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>NH]Cl, while for the GaCl<sub>3</sub>-complex a straightforward addition of the components is most convenient (eqn. (3), (4)).

$$\begin{array}{l} \text{Li}[\text{GaH}_4] + [3,5\text{-Me}_2\text{-Py-H}]\text{Cl} \longrightarrow \\ \text{H}_3\text{Ga}(3,5\text{-Me}_2\text{-Py}) + \text{H}_2 + \text{Li}\text{Cl} \quad (3) \end{array}$$

$$(GaCl_3)_2 + 2 (3,5-Me_2-Py) \rightarrow 2 Cl_3Ga(3,5-Me_2-Py)$$
 (4)

The 1 : 1-complexes of  $HGaCl_2$  and  $GaCl_3$  with pyridines are obtained from the reactions of equimolar quantities of the components. An excess of pyridines leads to the formation of 1 : 2-complexes as demonstrated for the 3,5-dimethylpyridine case (eqn. (5)).

$$(HGaCl_2)_2 + 4 Py \rightarrow 2 HCl_2Ga(Py)_2$$
(5)

This 1 : 2 adduct was isolated in pure, crystalline form and its IR-spectrum was found to exhibit the absorption band for a Ga–H stretching vibration. Any deprotonation by the second mole of pyridine base can therefore be excluded. As shown by an X-ray diffraction study, the compound has a trigonal-bipyramidal configuration with a pentacoordinate gallium atom (below). GaCl<sub>3</sub> is also known to form a 1 : 2 complex with pyridines,<sup>11</sup> which indicates that both HGaCl<sub>2</sub>(Py) and GaCl<sub>3</sub>(Py) have sufficient acceptor character towards pyridines. It should be noted, however, that the 1 : 2 complex of net stoichiometry {GaCl<sub>3</sub>(Py)<sub>2</sub>} was in fact found to be an ionic compound <sup>11</sup> with the ligands redistributed to give [Cl<sub>2</sub>Ga(Py)<sub>4</sub>]<sup>+</sup>-[GaCl<sub>4</sub>]<sup>-</sup>.

The tetrachlorogallate anion in salts  $M[GaCl_4]$  appears to be devoid of acceptor properties. It has now been observed that pyridinium tetrachlorogallate  $[Py-H]^+[GaCl_4]^-$  adds a second equivalent of pyridine, but the additional donor is accepted by the cation through hydrogen bonding (eqn. (6)).

$$[Py-H]^{+}[GaCl_{4}]^{-} + Py \longrightarrow [Py-H \cdots Py]^{+}[GaCl_{4}]^{-}$$
(6)

The structure of  $[Py-H \cdots Py]GaCl_4$  has been determined and the anion shown to be an undistorted tetrahedron (below).

### Structural studies

Crystals of [Py-H][GeCl<sub>3</sub>] are monoclinic, space group  $P2_1/c$ , with Z = 4 formula units in the unit cell. The asymmetric unit contains one pyridinium cation and one trichlorogermanate(II) anion (Fig. 1). The GeCl<sub>3</sub><sup>-</sup> anion has a pyramidal geometry reminiscent of the structure of the molecular analogue AsCl<sub>3</sub>. The three Ge–Cl distances are in the range 2.301(1)–2.325(1) Å, the three angles Cl–Ge–Cl in the range 93.72(4)–96.00(4)°. Deviations from idealized  $C_{3v}$  symmetry are therefore quite small. The data also compare well with dimensions found in



**Fig. 1** Molecular structure of  $[Py-H]^+[GeCl_3]^-$  showing the pyramidal geometry of the  $[GeCl_3]^-$  anion. Selected bond lengths [Å] and angles [<sup>a</sup>]: Ge(1)–Cl(1) 2.301(1), Ge(1)–Cl(2) 2.322(1), Ge(1)–Cl(3) 2.325(1); Cl(1)–Ge(1)–Cl(2) 93.72(4), Cl(1)–Ge(1)–Cl(3) 96.00(4), Cl(2)–Ge(1)–Cl(3) 94.75(4).

other trichlorogermanate( $\pi$ ) salts.<sup>3</sup> The pyridinium cation shows no anomalies. The distances from the N–H group to neighbouring Cl atoms are large and do not indicate significant hydrogen bonding.

The crystallographic data for the 1 : 1 adducts of  $HGaCl_2$  with Py, 4-Me<sub>2</sub>N-Py, 4-NC-Py, and 3,5-Me<sub>2</sub>-Py have been summarized in Table 1. All of these crystals contain neutral molecules, the structures of which are shown in Figs. 2–5. Because of many similarities among the members of this group of compounds, only the structure of  $HGaCl_2(Py)$  is discussed as a reference in more detail.

The crystals of  $HGaCl_2(Py)$  are the only phase to contain two independent molecules in the asymmetric unit, but the two



Fig. 2 Molecular structure of  $HGaCl_2(Py)$ . The two independent molecules in the asymmetric unit are shown. Selected bond lengths [Å] and angles [°]: Ga(1)-Cl(1) 2.1928(6), Ga(1)-Cl(2) 2.1895(6), Ga(1)-N(11) 2.000(2), Ga(1)-H(1) 1.45(3), Ga(2)-Cl(3) 2.1893(6), Ga(2)-Cl(4) 2.1847(7), Ga(2)-N(21) 1.998(2), Ga(2)-H(2) 1.47(3); Cl(1)-Ga(1)-Cl(2) 107.76(3), Cl(1)-Ga(1)-H(1) 115(1), Cl(2)-Ga(1)-H(1) 117(1), N(11)-Ga(1)-Cl(1) 100.85(6), N(11)-Ga(1)-Cl(2) 103.82(6), N(11)-Ga(1)-H(1) 111(1), Cl(3)-Ga(2)-Cl(4) 107.37(3), Cl(3)-Ga(2)-H(2) 119.9(9), Cl(4)-Ga(2)-H(2) 112(1), N(21)-Ga(2)-Cl(3) 102.06(6), N(21)-Ga(2)-Cl(4) 103.08(6), N(21)-Ga(2)-H(2) 111(1).



Fig. 3 Molecular structure of  $HGaCl_2(4-Me_2N-Py)$ . Selected bond lengths [Å] and angles [°]: Ga(1)-Cl(1) 2.2021(5), Ga(1)-Cl(2) 2.1937(5), Ga(1)-N(11) 1.971(2), Ga(1)-H(1) 1.46(3); Cl(1)-Ga(1)-Cl(2) 105.67(2), Cl(1)-Ga(1)-H(1) 115(1), Cl(2)-Ga(1)-H(1) 117.2(9), N(11)-Ga(1)-Cl(1) 103.34(5), N(11)-Ga(1)-Cl(2) 104.41(5), N(11)-Ga(1)-H(1) 109.8(9).

	[Py-H][GeCl <sub>3</sub> ]	HGaCl <sub>2</sub> (Py)	HGaCl <sub>2</sub> (4-Me <sub>2</sub> N-Py)	HGaCl <sub>2</sub> (4-NC-Py)	HGaCl <sub>2</sub> (3,5-Me <sub>2</sub> -Py)	
Empirical formula	C₅H <sub>6</sub> Cl₃GeN	C5H6Cl2GaN	C7H11Cl2GaN2	C <sub>6</sub> H <sub>5</sub> Cl <sub>2</sub> GaN <sub>2</sub>	C7H10Cl2GaN	
M	259.05	220.73	263.80	245.74	248.78	
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	
Space group	$P2_1/c$	$P\overline{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$	
a/Å	8.8187(2)	7.9436(2)	7.3133(1)	10.4429(7)	8.1301(2)	
b/Å	9.3672(2)	8.5157(2)	16.9338(3)	8.3052(3)	9.1466(2)	
c/Å	11.3129(2)	13.4892(4)	8.5934(2)	11.0553(7)	13.7748(4)	
a/°	90	86.5446(11)	90	90	90	
βl°	101.4859(19)	74.6191(13)	96.9279(7)	104.466(3)	101.9204(12)	
$\gamma l^{\circ}$	90	65.1942(15)	90	90	90	
V/Å <sup>3</sup>	915.80(3)	797.27(4)	1056.45(3)	928.43(9)	1002.24(4)	
$\rho_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.879	1.839	1.659	1.758	1.649	
Z	4	4	4	4	4	
<i>F</i> (000)	504	432	528	480	496	
$\mu$ (Mo-K <sub>a</sub> )/cm <sup>-1</sup>	41.47	40.32	30.60	34.76	32.18	
T/K	143	143	143	143	143	
Refls. measured	21681	20638	22853	11088	28989	
Refls. unique	$1614 [R_{int} = 0.034]$	2738 $[R_{int} = 0.024]$	$1833 [R_{int} = 0.024]$	$1624 [R_{int} = 0.025]$	$1830 [R_{int} = 0.039]$	
Refined parameters/restraints	95/0	211/0	153/0	120/0	140/0	
$R1 \left[I \ge 2\sigma(I)\right]$	0.0321	0.0232	0.0208	0.0230	0.0242	
$wR2^a$	0.0823	0.0621	0.0587	0.0617	0.0637	
Weighting scheme	a = 0.0198,	a = 0.0261,	a = 0.0312,	a = 0.0271,	a = 0.0301,	
0 0	<i>b</i> = 3.0188	b = 0.5820	b = 0.4095	b = 0.4392	b = 0.5653	
$\sigma_{\rm fin}({ m max/min})/{ m e}~{ m \AA}^{-3}$	0.565/-0.520	0.395/-0.470	0.396/-0.231	0.347/-0.362	0.352/-0.418	
${}^{a} wR2 = \{ \sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}] \}^{1/2}; w = 1 / [\sigma^{2}(F_{o}^{2}) + (ap)^{2} + bp]; p = (F_{o}^{2} + 2F_{c}^{2}) / 3.$						



Fig. 4 Molecular structure of  $HGaCl_2(4-NC-Py)$ . Selected bond lengths [Å] and angles [°]: Ga(1)-Cl(1) 2.1878(6), Ga(1)-Cl(2) 2.1705(6), Ga(1)-N(1) 2.017(2), Ga(1)-H(1) 1.49(2); Cl(1)-Ga(1)-Cl(2) 107.77(2), Cl(1)-Ga(1)-H(1) 119.0(9), Cl(2)-Ga(1)-H(1) 116.4(9), N(1)-Ga(1)-Cl(1) 101.18(5), N(1)-Ga(1)-Cl(2) 100.53(5), N(1)-Ga(1)-H(1) 109.2(9).



structures are fully consistent as shown by the following comparison of the most accurate distances and angles: Ga1-N11 2.000(2), Ga2-N21 1.998(2), Ga1-Cl1 2.1928(6), Ga1-Cl2 2.1895(6), Ga2–Cl3 2.1893(6), Ga2–Cl4 2.1847(7) Å; Cl1–Ga1– Cl2 107.76(3)°, Cl3–Ga2–Cl4 107.37(3)°.

The Ga–H bond lengths and H–Ga–Cl angles are generally less accurate and found in the ranges 1.45(3) to 1.53(2) Å and 112(1) and 119.9(9)°, respectively, for all four complexes, in good agreement with a recent summary.<sup>12</sup> The gallium atoms have a distorted tetrahedral environment with no evidence for significant intermolecular interactions. The closest approach appears in HGaCl<sub>2</sub>(Py) for a pair of molecules related by a center of inversion (with the central atoms Ga1/Ga1'), where the distance Ga1–H1' is 3.199 Å and the angle Cl2–Ga1–H1' 176.5° (Fig. 6). The remainder of the angles, none of which is near to 90°, show very strong deviations from an idealized trigonal-bipyramidal geometry, and therefore this "pairing" should not be taken as a dimerization.



**Fig. 6** Shortest intermolecular Ga–H distances in the lattice of HGaCl<sub>2</sub>(Py) between two molecules related by a center of inversion.

Crystals of  $H_3Ga(3,5-Me_2-Py)$  contain two independent molecules in the asymmetric unit (Fig. 7). For one of the two molecules the three Ga-bound hydrogen atoms were located and refined, while for the other they were restrained to be equivalent (local  $C_3$  symmetry) in order to obtain meaningful results. The Ga–H bond lengths [in the range 1.49(4)–1.53(6) Å] are in good agreement with those observed for the HGaCl<sub>2</sub> complexes. The Ga–N distances Ga1–N11 2.073(4) and



Fig. 7 Molecular structure of  $H_3Ga(3,5-Me_2-Py)$ . The two independent molecules in the asymmetric unit are shown. Selected bond lengths [Å] and angles [°]: Ga(1)-H(11) 1.51(4), Ga(1)-H(12) 1.50(4), Ga(1)-H(13) 1.51(4), Ga(1)-N(11) 2.073(4), Ga(2)-H(21) 1.49(6), Ga(2)-H(22) 1.51(6), Ga(2)-H(23) 1.53(6), Ga(2)-N(21) 2.060(4); H(11)-Ga(1)-H(12) 117(1), H(11)-Ga(1)-H(13) 117(2), H(12)-Ga(1)-H(13) 118(1), N(11)-Ga(1)-H(11) 104(3), N(11)-Ga(1)-H(12) 98(2), N(11)-Ga(1)-H(13) 96(3), H(21)-Ga(2)-H(22) 114(3), H(21)-Ga(2)-H(23) 115(3), N(21)-Ga(2)-H(21) 106(2), N(21)-Ga(2)-H(22) 105(2), N(21)-Ga(2)-H(23) 102(2).

Ga2–N21 2.061(4) Å are significantly longer than those in the HGaCl<sub>2</sub> complexes [2.006(2) Å for HGaCl<sub>2</sub>(3,5-Me<sub>2</sub>-Py)] indicating the stronger acceptor character of dichlorogallane as compared to the chlorine-free gallane.

This suggestion is confirmed by the structure of  $Cl_3Ga-(3,5-Me_2-Py)$ , where the Ga–N distance is again shorter at 1.968(1) Å (Fig. 8). Otherwise this reference structure has no anomalies.



**Fig. 8** Molecular structure of  $Cl_3Ga(3,5-Me_2-Py)$ . The conformation approaches mirror symmetry (point group  $C_s$ ) with the virtual mirror plane passing through N(1), Ga(1) and Cl(2). Selected bond lengths [Å] and angles [°]: Ga(1)–Cl(1) 2.1608(5), Ga(1)–Cl(2) 2.1517(5), Ga(1)–Cl(3) 2.1610(4), Ga(1)–N(1) 1.968(1); Cl(1)–Ga(1)–Cl(2) 112.29(2), Cl(1)–Ga(1)–Cl(3) 112.19(2), Cl(2)–Ga(1)–Cl(3) 111.38(2), N(1)–Ga(1)–Cl(1) 106.55(4), N(1)–Ga(1)–Cl(2) 108.17(4), N(1)–Ga(1)–Cl(3) 105.85(4).

Crystals of the 1 : 2 complex HGaCl<sub>2</sub>(3,5-Me<sub>2</sub>-Py)<sub>2</sub> feature molecules with a trigonal bipyramidal structure in which the chlorine atoms and the hydrogen atom occupy the equatorial positions (Fig. 9). The geometry has no crystallographically imposed symmetry, but the arrangement shows only small deviations from the maximum attainable symmetry of point group  $C_{2v}$ , the twofold axis running through the Ga–H bond [Ga–H 1.51(3) Å]. The Ga–Cl and Ga–N distances are equal within the limits of standard deviations, and the angle N–Ga–N is close to linear [179.28(7)°]. Surprisingly, the Cl–Ga–Cl angle is only



Fig. 9 Molecular structure of  $HGaCl_2(3,5-Me_2-Py)_2$ . The arrangement shows only small deviations from the maximum attainable symmetry of point group  $C_{2v}$ , with the twofold axis running through the Ga–H bond and the mirror plane passing through N(11), Ga(1), H(1) and N(21). Selected bond lengths [Å] and angles [°]: Ga(1)–Cl(2) 2.2214(7), Ga(1)–Cl(3) 2.2237(8), Ga(1)–N(11) 2.196(2), Ga(1)–N(21) 2.188(2), Ga(1)–H(1) 1.51(3); Cl(2)–Ga(1)–Cl(3) 111.38(4), N(11)–Ga(1)–N(21) 179.28(7), Cl(2)–Ga(1)–H(1) 125(1), Cl(3)–Ga(1)–H(1) 123(1), N(11)–Ga(1)–Cl(2) 89.55(6), N(11)–Ga(1)–Cl(3) 89.77(6), N(11)–Ga(1)–H(1) 91(1), N(21)–Ga(1)–Cl(2) 90.85(6), N(21)–Ga(1)–Cl(3) 89.52(6), N(21)–Ga(1)–H(1) 89(1).

111.38(4)°, while the two H–Ga–Cl angles are larger than the trigonal bipyramidal standard (120°): 125(1)° and 123(1)°. The sum of the equatorial angles is exactly 360°. The axial Ga–N distances of 2.188(2) and 2.196(2) Å in the 1 : 2 complex are almost 10% larger than the Ga–N distances in all of the 1 : 1 complexes of HGaCl<sub>2</sub> (above). If the rule is accepted that shorter bonds are generally stronger, bonding of the first ligand L in the 1 : 1 complexes is thus much tighter than any of the two donor/acceptor bonds in the 1 : 2 complex. The two pyridine rings are almost coplanar.

It should be remembered that the 1 : 2 adduct  $\{GaCl_3(Py)_2\}$  has the ionic structure  $[Cl_2Ga(Py)_4][GaCl_4]$ . There is presently no evidence for a similar ligand redistribution in the complex of HGaCl<sub>2</sub> with 2 equivalents of 3,5-Me<sub>2</sub>-Py, possibly involving  $[H_2Ga(Py)_4][GaCl_4]$ .

Crystals of  $[Py-H \cdots Py]^+[GaCl_4]^-$  are orthorhombic, space group  $Cmc2_1$ , with Z = 4 formula units in the unit cell. The asymmetric unit contains one half of the anion and one half of each of the pyridines, the remainder being generated by symmetry operations. The anion geometry is based on a slightly distorted tetrahedron, while the pairs of pyridine rings are almost coplanar and connected *via* a N–H–N hydrogen bond: N21–H21A 0.95(8), H21A–N11 1.77(8), N21–N11 2.706(6) Å, N21–H21A–N11 169(6)° (Fig. 10). The stacking of the anions and the columns of cations is illustrated in Fig. 11.

# Conclusions

Trichlorogermane HGeCl<sub>3</sub> and dichlorogallane HGaCl<sub>2</sub> (and its adducts) were found to react with pyridines in an entirely different way. Even the weak base pyridine is able to deprotonate HGeCl<sub>3</sub> to give a pyridinium salt with trigonal-pyramidal trichlorogermanate(II) anions containing germanium in its oxidation state +II. Since pyridine in its action as a base should not be considered a reducing agent, HGeCl<sub>3</sub> must also be assigned the +II oxidation state for its central atom owing to the unusual polarization (+)H–Ge(-) of its Ge–H bond.

By contrast, HGaCl<sub>2</sub> forms 1 : 1 or 1 : 2 addition compounds with pyridines, which have standard pseudo-tetrahedral [HGa-Cl<sub>2</sub>(L)] or trigonal-bipyramidal structures [HGaCl<sub>2</sub>(L)<sub>2</sub>]. No deprotonation is observed even with an excess of pyridine base, and no ligand redistribution to give ionic isomers<sup>9</sup> occurs. Thus while (GaCl<sub>3</sub>)<sub>2</sub> formally reacts more often than not out of an ionic form [GaCl<sub>2</sub>]<sup>+</sup>[GaCl<sub>4</sub>]<sup>-</sup>, there are presently no examples



Fig. 10 Molecular structure of  $[Py-H \cdots Py]^+[GaCl_4]^-$ . The asymmetric unit contains one half of the anion and one half of each of the pyridines, the remainder being generated by symmetry operations. The two pyridines are related by a strong hydrogen bond. Selected bond lengths [Å] and angles [°]: Ga(1)–Cl(1) 2.173(1), Ga(2)–Cl(2) 2.187(1), Ga(3)–Cl(3) 2.1774(9), N(21)–H(21A) 0.95(8), H(21A)–N(11) 1.77(8); Cl(1)–Ga(1)–Cl(2) 108.91(6), Cl(1)–Ga(1)–Cl(3) 109.49(4), Cl(2)–Ga(1)–Cl(3) 108.79(4), Cl(3)–Ga(1)–Cl(3)'111.34(5), N(21)–H(21A)–N(11) 169(6).



Fig. 11 The stacking of the anions and the columns of cations in the lattice of  $[Py-H \cdots Py]^+[GaCl_4]^-$ .

where  $(HGaCl_2)_2$  would appear to function as  $[GaH_2]^+[GaCl_4]^-$  towards donor molecules.

The structures of the 1 : 1 complexes are similar to those of the corresponding adducts of the types  $Cl_3Ga(L)$  or  $H_3Ga(L)$ , for which two prototypes have also been prepared and investigated. However, tetrachlorgallate(III) anions  $[GaCl_4]^-$  have no acceptor character, and with  $[Py-H]^+[GaCl_4]^-$  excess pyridine becomes attached to the cation *via* hydrogen bonding:  $[Py-H \cdots Py]^+[GaCl_4]^-$ .

The results have thus shown that conversion of HGeCl<sub>3</sub> (with tetracoordinate germanium atoms) into lower-coordinate Ge(II) compounds is a facile process, which can be accomplished even with a very weak base. By contrast, the analogous transformation of HGaCl<sub>2</sub> into Ga(I) compounds is not easily induced. Action of even strong base is not sufficient, probably because of the inherent polarization (-)H-Ga(+) which is the opposite of (+)H-Ge(-). It should be noted, however, that neat (HGaCl<sub>2</sub>)<sub>2</sub> is readily thermolized at slightly above room temperatures to give hydrogen gas<sup>7a-e</sup> and Ga[GaCl<sub>4</sub>] containing one of the two gallium atoms in the +1 oxidation state. This process is an example of reductive elimination of substrate (H<sub>2</sub>) from the gallium(III) center in (HGaCl<sub>2</sub>)<sub>2</sub>. Mechanistically, the process may involve elimination of HCl followed by a reaction with a second H-Ga function to give molecular hydrogen.

The coordination chemistry of  $HGeCl_3$ ,<sup>13</sup> and  $(HGaCl_2)_2$  with tertiary phospines will be the subject of a forthcoming report.<sup>14</sup>

## **Experimental**

All experiments were carried out in an atmosphere of dry and pure nitrogen. Glassware was oven-dried and filled with nitrogen, and solvents and the pyridines were dried following established procedures and saturated with nitrogen. Conventional equipment was used throughout. Anhydrous (GaCl<sub>3</sub>)<sub>2</sub> and the pyridines were commercially available. (HGaCl<sub>2</sub>)<sub>2</sub> was prepared employing a published method recently improved to make it more convenient.<sup>7d</sup> LiGaH<sub>4</sub> and HGeCl<sub>3</sub> were prepared according to literature procedures.<sup>15,16</sup>

#### Syntheses

**Pyridinium trichlorogermanate(II), [Py-H][GeCl<sub>3</sub>].** Freshly prepared HGeCl<sub>3</sub> (2.0 g, 11.1 mmol) is cooled to -40 °C and slowly dissolved in 10 ml of freshly distilled and then precooled pyridine (9.60 mmol). The reaction mixture is slowly warmed to room temperature, excess pyridine is removed in a vacuum, and the colourless, hygroscopic residue is recrystallized from toluene; 2.8 g (97% yield), mp 114 °C (decomp.). <sup>1</sup>H-NMR (CD<sub>3</sub>CN, 20 °C):  $\delta$  2.45, br s, 1H, NH; 8.17, dd, J 6.56 and 7.84 Hz, 2H, CH<sub>(3/5)</sub>; 8.71, t, J 7.85 Hz, 1H, CH<sub>(4)</sub>; 8.85, d, J 6.57 Hz, 2H, CH<sub>(2/6)</sub>. <sup>13</sup>C{<sup>1</sup>H}-NMR:  $\delta$  129.1, s, 2C, C<sub>(3/5)</sub>; 142.7, s, 1C, C<sub>(4)</sub>; 148.8, s, 2C, C<sub>(2/6)</sub>. Analysis found C 24.17, H 2.48, N 5.57, Cl 40.53; C<sub>5</sub>H<sub>6</sub>NGeCl<sub>3</sub> (259.08) requires C 23.18, H 2.33, N 5.41, Cl 41.05%.

**Bis(4-ethyl-pyridine)tetrachlorogermane,** (4-Et-Py)<sub>2</sub>GeCl<sub>4</sub>. GeCl<sub>4</sub> (2.0 g, 1.06 ml, 9.33 mmol) is reacted with 4-ethylpyridine (2.0 g, 2.04 ml, 18.7 mmol) in 10 ml of toluene with stirring at 20 °C. All volatiles are removed in a vacuum to leave a colourless solid; 3.97 g (97% yield), mp 118 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 20 °C):  $\delta$  1.32, t, J 7.67 Hz, 3H, Me; 2.86, q, 2H, CH<sub>2</sub>; 7.61, d, J 6.18 Hz, 2H, CH<sub>3/5</sub>; 8.63, d, 2H, CH<sub>2/6</sub>. Analysis found C 39.52, H 4.48, N 6.57, Cl 33.53; C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>GeCl<sub>4</sub> (428.73) requires C 39.22, H 4.23, N 6.53, Cl 33.08%.

**Pyridine-pyridinium tetrachlorogallate(III), [Py-H···Py]-[GaCl<sub>4</sub>].** GaCl<sub>3</sub> is dissolved (2.00 g, 5.68 mmol) in 10 ml of dry pyridine, and pyridium chloride (1.32 g, 11.42 mmol) is dissolved in 30 ml of the same solvent. From the combined solutions excess pyridine is removed in a vacuum after 1 h and the residue is crystallized from toluene; 4.00 g (95% yield), mp 116 °C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  7.78, m, 2H, CH<sub>(3/5)</sub>; 8.28, m, 1H, CH<sub>(4)</sub>; 8.71, m, 2H, CH<sub>(2/6)</sub>. <sup>13</sup>C{<sup>1</sup>H}-NMR:  $\delta$  125.1, s, 2C, C<sub>(3/5)</sub>; 141.7, s, 1C, C<sub>(4)</sub>; 145.0, s, 2C, C<sub>(2/6)</sub>. Analysis found C 32.83, H 3.00, N 7.67, Cl 37.34; C<sub>10</sub>H<sub>11</sub>N<sub>2</sub>GaCl<sub>4</sub> (370.73) requires C 32.40, H 2.99, N 7.67, Cl 38.25%.

Pyridine-dichlorogallane, 3,5-dimethyl-pyridine-dichlorogallane and 4-cyano-pyridine-dichlorogallane, HGaCl<sub>2</sub>(Py), HGaCl<sub>2</sub>(3,5-Me<sub>2</sub>-Py) and HGaCl<sub>2</sub>(4-NC-Py). Freshly prepared (HGaCl<sub>2</sub>)<sub>2</sub> (2.12 g, 7.48 mmol of dimer) is dissolved in 30 ml of dry diethyl ether at -78 °C. To this solution one equivalent of the ligand (1.18 g, 14.9 mmol for pyridine, 1.60 g, 14.9 mmol for 3,5-dimethylpyridine and 1.55 g, 14.9 mmol for 4-cyanopyridine) dissolved in 10 ml of dry diethyl ether is added slowly at this temperature (an excess of ligand should be avoided in any case in order to prevent the formation of [HGaCl<sub>2</sub>(L)<sub>2</sub>]type complexes). After the addition is completed, a colourless precipitate forms, which redissolves upon warming to room temperature and stirring for 1 h. Storage on dry ice over night yields the product in the form of colourless crystals. The solution is filtered off and the remainder of the product obtained by removing about two thirds of the solvent from the filtrate and

	$H_3Ga(3,5-Me_2-Py)$	$Cl_3Ga(3,5-Me_2-Py)$	$HGaCl_2(3,5-Me_2-Py)_2$	[Py-H ··· Py][GaCl₄]
Empirical formula	C5H12GaN	C7H9Cl3GaN	C <sub>14</sub> H <sub>19</sub> Cl <sub>2</sub> GaN <sub>2</sub>	C <sub>10</sub> H <sub>11</sub> Cl <sub>4</sub> GaN <sub>2</sub>
M	179.90	283.22	355.84	370.73
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P\overline{1}$	$P2_1/c$	$Cmc2_1$
aĺÅ	8.9394(3)	7.1968(1)	11.0572(3)	9.0480(4)
b/Å	13.8205(5)	9.1925(2)	10.2092(3)	12.1395(7)
c/Å	14.0935(5)	9.4850(2)	14.7805(6)	13.4546(6)
<i>a</i> /°	90	87.3256(7)	90	90
βl°	95.1123(15)	71.9435(8)	94.1991(11)	90
y/°	90	68.3327(12)	90	90
V/Å <sup>3</sup>	1734.28(11)	552.805(18)	1664.02(9)	1477.83(13)
$\rho_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.378	1.702	1.421	1.666
Ζ	8	2	4	4
F(000)	736	280	728	736
$\mu$ (Mo-K <sub>a</sub> /cm <sup>-1</sup>	30.94	31.162	19.63	25.64
T/K	143	143	143	143
Refls. measured	56453	15084	38639	22132
Refls. unique	$3127 [R_{int} = 0.048]$	2374 $[R_{int} = 0.029]$	2930 $[R_{int} = 0.036]$	1367 $[R_{int} = 0.070]$
Refined parameters/restraints	191/6	145/0	248/0	110/1
$R1 \left[I \ge 2\sigma(I)\right]$	0.0463	0.0234	0.0352	0.0260
$wR2^a$	0.1258	0.0642	0.0931	0.0560
Weighting scheme	a = 0.0453, b = 4.1443	a = 0.0324, b = 0.2125	<i>a</i> = 0.0467, <i>b</i> = 1.5954	a = 0.0057, b = 1.5245
$\sigma_{\rm fin}({\rm max/min})/{\rm e}~{\rm \AA}^{-3}$	0.869/-0.453	0.489/-0.311	0.441/-0.476	0.328/-0.531
$a w R^2 = \{ \sum [w(F^2 - F^2)^2] / \sum [w(F^2)^2] \}$	$1^{1/2} w = 1/[\sigma^2(F^2) + (an)^2 + h^2]$	$pn$ ]: $n = (F^2 + 2F^2)/3$		

Table 2 Crystal data, data collection, and structure refinement of  $H_3Ga(3,5-Me_2-Py)$ ,  $Cl_3Ga(3,5-Me_2-Py)$ ,  $HGaCl_2(3,5-Me_2-Py)_2$  and  $[Py-H\cdots Py][GaCl_4]$ 

storing the residue on dry ice over night (overall yields are 93 to 95%).

*HGaCl*<sub>2</sub>(*Py*). <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ 6.18, m, AA'BB'C, 2H, CH<sub>(3/5)</sub>; 6.57, t, J 7.92 Hz, 1H, CH<sub>(4)</sub>; 7.99, d, J 4.94 Hz, 2H, CH<sub>(2/6)</sub>; not detected: GaH. <sup>13</sup>C{<sup>1</sup>H}-NMR: δ 125.5, s, 2C, C<sub>(3/5)</sub>; 141.0, s, 1C, C<sub>(4)</sub>; 146.3, s, 2C, C<sub>(2/6)</sub>. Analysis found C 26.87, H 2.90, N 6.25, Cl 31.81; C<sub>5</sub>H<sub>6</sub>NGaCl<sub>2</sub> (220.74) requires C 27.21, H 2.74, N 6.35, Cl 32.12%. IR (Nujol mull/cm<sup>-1</sup>): 1970 [Ga–H], 1613 s, 1488 m, 1248 w, 1216 m, 1160 m, 1070 s, 1051 s, 1015 s, 883 w, 761 s, 652 s, 605 s, 588 s.

*HGaCl*<sub>2</sub>(3,5-*Me*<sub>2</sub>-*Py*). mp 66 °C (decomp.); <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.37, s, 6H, Me<sub>(3/5)</sub>; 6.28, s, 1H, CH<sub>(4)</sub>; 7.97, s, 2H, CH<sub>(2/6)</sub>; not detected: GaH. <sup>13</sup>C{<sup>1</sup>H}-NMR: δ 17.5, s, 2C, Me<sub>(3/5)</sub>, 135.6, s, 2C, C<sub>(3/5)</sub>; 142.2, s, 1C, C<sub>(4)</sub>; 144.0, s, 2C, C<sub>(2/6)</sub>. Analysis found C 34.31, H 4.15, N 5.83, Cl 27.50; C<sub>7</sub>H<sub>10</sub>-NGaCl<sub>2</sub> (248.79) requires C 33.79, H 4.05, N 5.63, Cl 28.02%. IR (Nujol mull/cm<sup>-1</sup>): 1978 [Ga–H], 1611 s, 1285 s, 1251 s, 1175 s, 1149 s, 1046 s, 945 m, 867 s, 791 s, 697 m, 621 m, 540 m.

*HGaCl*<sub>2</sub>(*4*-*NC*-*Py*). mp 51 °C (decomp.), <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  5.97, d, J 5.69 Hz, 2H, CH<sub>(3/5)</sub>; 7.82, d, J 5.69 Hz, 2H, CH<sub>(2/6)</sub>; not detected: GaH. <sup>13</sup>C{<sup>1</sup>H}-NMR:  $\delta$  127.0, s, 2C, C<sub>(3/5)</sub>; 147.4, s, 2C, C<sub>(2/6)</sub>; not detected: C<sub>(4)</sub> and CN<sub>(4)</sub>. Analysis found C 30.26, H 2.14, N 11.67, Cl 27.40; C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>GaCl<sub>2</sub> (245.75) requires C 29.32, H 2.05, N 11.40, Cl 28.85%. IR (Nujol mull/ cm<sup>-1</sup>): 2239 w [C≡N], 1977 m [Ga–H], 1620 m, 1548 m, 1221 m, 1122 w, 1064 m, 1038 m, 970 w, 835 m, 797 w, 777 w, 728 w, 608 m, 557 m.

**Bis-(3,5-dimethyl-pyridine)-dichlorogallane,** HGaCl<sub>2</sub>(3,5-Me<sub>2</sub>-Py)<sub>2</sub>. To a solution of HGaCl<sub>2</sub>(3,5-Me<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N) (0.36 g, 1.5 mmol) in 25 ml of diethyl ether is added an excess of liquid 3,5-dimethyl-pyridine (0.17 g, 1.6 mmol) at room temperature. The solution is stirred for 2 h and then cooled to -78 °C over night. A colourless precipitate is obtained, which is filtered off and dried *in vacuo*. Crystals can be obtained from acetonitrile at -25 °C. 0.46 g (87% yield). <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.60, s, 12H, Me<sub>(3/5)</sub>; 6.51, s, 2H, CH<sub>(4)</sub>; 8.15, s, 4H, CH<sub>(2/6)</sub>; not detected: GaH. <sup>13</sup>C{<sup>1</sup>H}-NMR: δ 17.7, s, 4C, Me<sub>(3/5)</sub>, 134.1, s, 4C, C<sub>(3/5)</sub>; 139.7, s, 2C, C<sub>(4)</sub>; 145.9, s, 4C, C<sub>(2/6)</sub>. Analysis found C 46.87, H 5.21, N 7.73, Cl 20.26; C<sub>14</sub>H<sub>19</sub>N<sub>2</sub>GaCl<sub>2</sub> (355.84) requires C 47.24, H 5.38, N 7.87, Cl 19.92%. IR (Nujol mull/cm<sup>-1</sup>): 1873 [Ga–H], 1601 s, 1277 w, 1254 w, 1177 m, 1148 s, 1046 m, 1034 m, 943 w, 868 s, 822 m, 736 s, 700 s, 551 m.

**4-Dimethylamino-pyridine-dichlorogallane, HGaCl<sub>2</sub>(4-Me<sub>2</sub>N-Py).** The compound is prepared following the conventional route (above). Due to the limited solubility of the product in diethyl ether, the reaction mixture is filtered immediately after warming to room temperature and the complex is obtained as a colourless solid. Higher yields are obtained after storing the filtrate on dry ice over night (yield 95%); mp 232 °C (decomp.). <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.94, s, 6H, Me<sub>(N)</sub>; 5.52, d, J 7.32 Hz, 2H, CH<sub>(3/5)</sub>; 7.84, d, J 7.32 Hz, 2H, CH<sub>(2/6)</sub>; not detected: GaH. <sup>13</sup>C{<sup>1</sup>H}-NMR: δ 38.3, s, 2C, C<sub>(N)</sub>; 106.8, s, 2C, C<sub>(3/5)</sub>; 145.0, s, 2C, C<sub>(2/6)</sub>; not detected: C<sub>(4)</sub>. Analysis found C 32.52, H 4.33, N 10.76, Cl 26.16; C<sub>7</sub>H<sub>11</sub>N<sub>2</sub>GaCl<sub>2</sub> (263.81) requires C 31.87, H 4.20, N 10.62, Cl 26.88%. IR (Nujol mull/cm<sup>-1</sup>): 1979 m [Ga–H], 1625 s, 1558 s, 1526 w, 1306 w, 1232 s, 1120 w, 1073 s, 1026 s, 946 w, 816 s, 725 w, 616 s, 559 m, 523 m.

3,5-Dimethyl-pyridine-gallane, H<sub>3</sub>Ga(3,5-Me<sub>2</sub>-Py). This compound was prepared by a variation of literature procedures.<sup>17</sup> To a solution of freshly prepared LiGaH<sub>4</sub> (0.89g, 11.0 mmol) in 30 ml of dry diethyl ether kept at -78 °C is added a substoichiometric amount of 3,5-dimethyl-pyridinium-chloride (10.4 mmol, 1.49 g) in small portions under nitrogen. The resulting slurry is allowed to warm to ambient temperature over a period of 5 h and is stirred for a further 2 h. Upon warming gas evolution is observed. The suspension is filtered and about half of the solvent is removed in vacuo. Crystals are obtained by slow cooling of the remaining solution to -78 °C over night. The solution is filtered, and the crystals are dried in vacuo. Higher yields are obtained by removing most of the solvent and cooling to -78 °C (yield 71%). The product decomposes slowly at room temperature, but can be stored without decomposition at -25 °C; mp 67 °C (fast decomp.). <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.43, s, 6H, Me<sub>(3/5)</sub>; 5.64, br s, 3H, GaH; 6.34, s, 1H, CH<sub>(4)</sub>; 7.97, s, 2H,  $CH_{(2/6)}$ . <sup>13</sup>C{<sup>1</sup>H}-NMR:  $\delta$  17.4, s, 2C,  $Me_{(3/5)}$ ; 134.7, s, 2C,  $C_{(3/5)}$ ; 140.1, s, 1C, C<sub>(4)</sub>; 146.1, s, 2C, C<sub>(2/6)</sub>. Analysis found C 46.00, H 6.30, N 7.62; C<sub>7</sub>H<sub>12</sub>NGa (179.90) requires C 46.73, H 6.72, N 7.79%. IR (Nujol mull/cm<sup>-1</sup>): 1822 s [Ga-H], 1604 m, 1279 w, 1254 w, 1166 m, 1137 w, 1036 w, 867 m, 786 s, 725 s, 700 s, 548 m.

**3,5-Dimethyl-pyridine-gallium-trichloride,**  $Cl_3Ga(3,5-Me_2-Py)$ . (GaCl<sub>3</sub>)<sub>2</sub> (2.71 g, 7.69 mmol of dimer) is dissolved in 20 ml of cold diethyl ether and neat 3,5-dimethyl-pyridine (1.65 g,

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15.38 mmol) is added dropwise at -30 °C. The solution is stirred for 2 h and then, after evaporating about half of the solvent in a vacuum, cooled to  $-7\overline{8}$  °C over night. Colourless crystals are obtained, the solution is filtered off and the product dried in vacuo (yield: 98%); mp 93–96 °C. <sup>1</sup>H-NMR ( $C_6D_6$ ): δ 1.33, s, 6H, Me<sub>(3/5)</sub>; 6.24, s, 1H, CH<sub>(4)</sub>; 8.01, s, 2H, CH<sub>(2/6)</sub>. <sup>13</sup>C{<sup>1</sup>H}-NMR: δ 17.5, s, 2C, Me<sub>(3/5)</sub>; 136.7, s, 2C, C<sub>(3/5)</sub>; 142.7, s, 1C, C<sub>(4)</sub>; 144.1, s, 2C, C<sub>(2/6)</sub>. Analysis found C 29.04, H 3.37, N 4.77, Cl 36.34; C7H9NGaCl3 (283.23) requires C 29.68, H 3.20, N 4.95, Cl 37.55%.

#### Determination of the crystal structures

Specimens of suitable quality and size of [Py-H][GeCl<sub>3</sub>], HGa-Cl<sub>2</sub>(Py), HGaCl<sub>2</sub>(4-Me<sub>2</sub>N-Py), HGaCl<sub>2</sub>(4-NC-Py), HGaCl<sub>2</sub>-(3,5-Me<sub>2</sub>-Py), H<sub>3</sub>Ga(3,5-Me<sub>2</sub>-Py), Cl<sub>3</sub>Ga(3,5-Me<sub>2</sub>-Py), HGaCl<sub>2</sub>- $(3,5-Me_2-Py)_2$  and  $[Py-H \cdots Py][GaCl_4]$  were mounted on the ends of quartz fibers in inert perfluoropolyalkyl ether and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo-K<sub>a</sub> radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix least-squares calculations on  $F^2$  (SHELXL-97).<sup>18</sup> The thermal motion was treated anisotropically for all nonhydrogen atoms. The C-H hydrogen atoms were calculated in ideal positions and allowed to ride on their parent atoms with fixed isotropic contributions in the structures of [Py-H][GeCl<sub>3</sub>], H<sub>2</sub>Ga(3,5-Me<sub>2</sub>-Py) and for one hydrogen atom in the structure of [Py-H ··· Py][GaCl<sub>4</sub>]. In all other structures the C-H hydrogen atoms were located and refined with isotropic displacement parameters. In H<sub>3</sub>Ga(3,5-Me<sub>2</sub>-Py) all three Ga-H and all three H-H distances were restrained to be equal for one of the two independent molecules (Ga1), for the other one (Ga2) no restraints were applied. The Flack parameter for [Py-H · · · Py][GaCl<sub>4</sub>] is 0.009(15). Absorption corrections for all structures except HGaCl<sub>2</sub>(3,5-Me<sub>2</sub>-Py) were carried out using DELABS, as part of the PLATON suite of programmes.19 Further informations on crystal data, data collection and structure refinement are summarized in Tables 1 and 2. CCDC reference numbers 211295-211303.

See http://www.rsc.org/suppdata/dt/b3/b305792e/ for crystal-

lographic data in CIF or other electronic format.

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