Synthesis and structures of gallium alkoxides†

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Homoleptic gallium tris(alkoxides) $[Ga(OR)_3]_2$ were prepared by the reaction of $[Ga(NMe_2)_3]_2$ (**1**) and excess ROH (R = $CH_2CH_2NMe_2$ (**2**), $CH(CH_3)CH_2NMe_2$ (**3**), $C(CH_3)_2CH_2OMe$ (**4**), CH_2CH_2OMe (**5**)) in toluene at room temperature. Compounds **2–5** were isolated as colourless oils. The side-products, $[Ga(OCH_2CH_2NMe_2)_2Cl]$ (**6**), $[Ga(OCH(CH_3)CH_2NMe_2)_2Cl]$ (**7**) and $[Ga(OC(CH_3)_2CH_2OMe)Cl_2]_2$ (**8**) were also isolated in low yield during the synthesis of **2**, **3** and **4**, respectively. However, compounds **6** and **7** were also prepared directly from the reaction of $[Ga(NMe_2)_2Cl]$ and 2 equivalents of ROH (**6**, R = $CH_2CH_2NMe_2$; **7**, R = $CH(CH_3)CH_2NMe_2$). Similarly, compound **8** was isolated from the reaction of $[Ga(NMe_2)Cl_2]$ and 1 equivalent of $HOC(CH_3)_2CH_2OMe$. Single crystal X-ray crystallography showed that the gallium bis(alkoxides) (**6** and **7**) are monomeric in the solid state with the gallium centre adopting a distorted trigonal bipyramidal geometry. In contrast, the gallium mono(alkoxide) **8** is dimeric.

Introduction

Group 13 diorganoalkoxometallanes are well known and a large number have been structurally characterised.[1] These complexes, $[R_2M(OR')]_n$ (M = Al, Ga, In; R, R′ = alkyl or aryl), are usually dimeric or trimeric and can be prepared *via* the reaction of R_3M with alcohol or salt elimination from the reaction of R_2MX and M′OR (M′ = alkali metal). In contrast, only a limited number of examples of organo-dialkoxometallanes have been reported in the literature.[2–5] These are rare species for gallium and indium, in contrast to the well known diorganoalkoxometallanes of gallium.[1] Until recently, the only structurally characterized example of an organodialkoxogallane incorporating a simple monodentate alkoxide group was $[HGa(O^tBu)_2]_2$.[2] In general, reaction of a gallane with two equivalents or an excess of alcohol does not yield the expected organodialkoxogallane, $[RM(OR')]_n$, in most cases. Instead reaction of Me_3M with an excess of alcohol often results in the formation of sesquialkoxides.[6,7] However, a dialkoxogallane incorporating donor functionalised ligands was prepared by the reaction of Et_3Ga with an excess of $HOCH_2CH_2NMe_2$ in toluene, under reflux conditions.[3] The structure of $[EtGa(OCH_2CH_2NMe_2)_2]$ was shown to be monomeric with the gallium centre adopting a distorted trigonal bipyramidal coordination geometry. More recently, similar reactions between Me_3Ga and two equivalents of ROH (R = Et, ^{n}Bu) in refluxing toluene afforded the methyldialkoxogallanes $[MeGa(OR)_2]_n$.[4] Both compounds adopt centrosymmetrical dimers which are connected to yield infinite chains along either [100] (R = Et) or [001] (R = ^{n}Bu).

A number of synthesis routes have been employed for the formation of homoleptic gallium alkoxides $[Ga(OR)_3]_n$.[1] The general procedures include reaction of gallium trihalide with NaOR, alkoxide/alcohol exchange, amine/alcohol exchange and transesterification reactions. Surprisingly few homoleptic gallium alkoxides have been structurally characterised, including $[Ga(O^iPr)_3]_3$, and $[Ga(OCMe_2Et)_3]_2$, although some ligand adducts of these complexes have been reported.[8–10]

We have been investigating the synthesis and characterisation of a range of gallium and indium alkoxides and their subsequent use as precursors to gallium and indium oxides (Ga_2O_3 and In_2O_3).[3,7,11–13] These materials find application as gas sensors (Ga_2O_3) and transparent conductors (In_2O_3). The use of diorganoalkoxogallanes resulted in the formation of oxygen deficient gallium oxide thin films on glass.[3] In an attempt to produce precursors which could form stoichiometric Ga_2O_3, we were interested in developing a range of organodialkoxogallanes and gallium tris(alkoxide)s, which possess a 1 : 2 and 1 : 3 ratio of Ga:O, respectively. The synthesis and characterisation of gallium alkoxides, of the type $[Ga(OR)_nCl_{3-n}]$, incorporating donor functionalised ligands (n = 3, R = $CH_2CH_2NMe_2$, $CH(CH_3)CH_2NMe_2$, $C(CH_3)_2CH_2OMe$, CH_2CH_2OMe; n = 2, R = $CH_2CH_2NMe_2$, $CH(CH_3)CH_2NMe_2$; n = 1, R = $C(CH_3)_2CH_2OMe$) is reported herein. The single crystal X-ray structures of three of the compounds, $[Ga(OCH_2CH_2NMe_2)_2Cl]$, $[Ga(OCH(CH_3)CH_2NMe_2)_2Cl]$ and $[Ga(OC(CH_3)_2CH_2OMe)Cl_2]_2$, are also reported (Scheme 1).

Results and discussion

Syntheses and characterization

Treatment of $[Ga(NMe_2)_3]_2$ (**1**) with an excess of ROH resulted in the formation of $[Ga(OR)_3]_2$ (R = $CH_2CH_2NMe_2$ (**2**), $CH(CH_3)CH_2NMe_2$ (**3**), $C(CH_3)_2CH_2OMe$ (**4**), CH_2CH_2OMe (**5**)). In each case an oil was isolated and initially no

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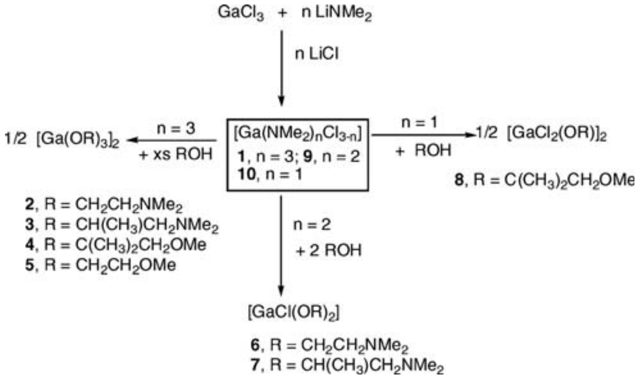

Scheme 1 Synthesis of compounds **1–10**.

crystalline solid formed. The dimeric nature of **2–5** was suggested by mass spectroscopy and also infrared spectroscopy, with absorptions at ~557 and 538 cm^{-1}, corresponding to Ga_2O_2 ring modes. A fluxional coordination of the donor heteroatom was indicated by the ^{1}H NMR spectra of **2–5** where the absence of proton coupling in the alkoxide ligand and broadening of the associated resonances was observed. We have previously described the synthesis of compounds **2** and **3**, which involved refluxing the reaction mixture for six hours. However, we have since found that this step is unnecessary and high yields of the compounds can be obtained from the same reaction at room temperature. Furthermore, on standing oils of **2** and **3** at room temperature for a few days, a small yield of colourless crystals was obtained. An X-ray crystallographic study was carried out on the colourless crystals (*vide supra*), which showed that the chlorodialkoxogallanes, $[Ga(OCH_2CH_2NMe_2)_2Cl]$ (**6**) and $[Ga(OCH(CH_3)CH_2NMe_2)_2Cl]$ (**7**), were afforded from oils of **2** and **3**, respectively. Similarly, crystals of the dimeric dichloroalkoxogallane $[Ga(OC(CH_3)CH_2OMe)Cl_2]_2$ (**8**) were obtained after standing the oil of compound **4** at room temperature for a few days. Unfortunately, crystals of **2–5** suitable for single crystal X-ray diffraction could not be isolated.

The isolation of gallium alkoxides contaminated with chloride has been observed previously.[14] The formation of **6–8** must be due to incomplete substitution of all the chloride ligands in the preparation of $[Ga(NMe_2)_3]_2$ **1**, resulting in the reaction of $[Ga(NMe_2)_nCl_{3-n}]$ ($n = 2$ for **6** and **7**; $n = 1$ for **8**) with ROH. These partially substituted compounds were only formed as minor impurities, as shown by the expected analytical and spectroscopic data obtained for compound **1** (Experimental section). Therefore, the reaction between $[Ga(NMe_2)_2Cl]$[15] (**9**) and two equivalents of ROH (R = $CH_2CH_2NMe_2$, $CH(CH_3)CH_2NMe_2$) was carried out in order to prepare compounds **6** and **7**, directly and in high yield. In both cases a pale yellow crystalline solid was isolated. Spectroscopic and analytical data indicated that the chlorodialkoxogallanes, $[Ga(OCH_2CH_2NMe_2)_2Cl]$ (**6**) and $[Ga(OCH(CH_3)CH_2NMe_2)_2Cl]$ (**7**) were formed (54–60% yield). A dative ligand–metal interaction in **6** and **7** was confirmed by a comparison of proton resonances of the alkoxide ligand in the product compared to the free ligand. Thus, in the ^{1}H NMR of **6** and **7** a downfield shift in the resonance of protons positioned α to the donor heteroatom is observed.

The reaction between $[Ga(NMe_2)Cl_2]$ (**10**) (prepared by the reaction of $GaCl_3$ and one equivalent of $LiNMe_2$ in toluene) and one equivalent of $HOC(CH_3)CH_2OMe$ was carried out in order to isolate compound **8** directly. Compound **8** was obtained as a pale yellow solid in high yield (Experimental section). Analytical and spectroscopic data for **8** was consistent with the formulation $[Ga(OC(CH_3)CH_2OMe)Cl_2]_2$ and the dimeric nature was confirmed by mass spectroscopy. The resonance of protons positioned α to the donor heteroatom showed a downfield shift, in the ^{1}H NMR spectrum of **8**, compared to the free ligand indicating a dative ligand–metal interaction. The structure of compound **8** is described below. These results show that although **6–8** were initially obtained as minor side-products they can be synthesised in high yield from the reaction of $[Ga(NMe_2)_nCl_{3-n}]$ and one or two equivalents of ROH. Furthermore, the reaction of $[Ga(NMe_2)_2Cl]$ and two equivalents of ROH provides a clean route to the novel gallium bis(alkoxide)s.

X-Ray crystallographic studies

The crystal structure of compound **6** was determined by single crystal X-ray diffraction and the results are shown in Fig. 1; selected bond lengths and angles are given in Table 1. Compound **6** crystallised into the orthorhombic space group $Pna2_1$. It is monomeric in the solid state with the gallium atom adopting a distorted trigonal bipyramidal geometry. The oxygen atoms of each alkoxide ligand and a chlorine atom occupy the equatorial positions while the N atoms of the NMe_2 group reside in the axial positions (Fig. 1). The Ga–N distances (av. 2.140 Å) are significantly shorter than the sum of the van der Waals radii and so indicative of a strong dative bonding interaction. Similar trigonal bipyramidal geometry at the gallium centre has been observed previously in the related intramolecularly stabilised alkoxogallanes $[EtGa(OCH_2CH_2NMe_2)_2]$ and $[ClGa(OR)_2]$ (R = $C(CF_3)_2CH_2C(CH_3){=}NMe$ and $C(CF_3)_2CH_2NMe_2$).[3,5] The Ga–O and Ga–N bond distances in these compounds are similar to those observed in **6**.

The structure of compound **7** was determined by single crystal X-ray crystallography, the results are shown in Fig. 2; selected bond lengths and angles are given in Table 1. Compound **7**

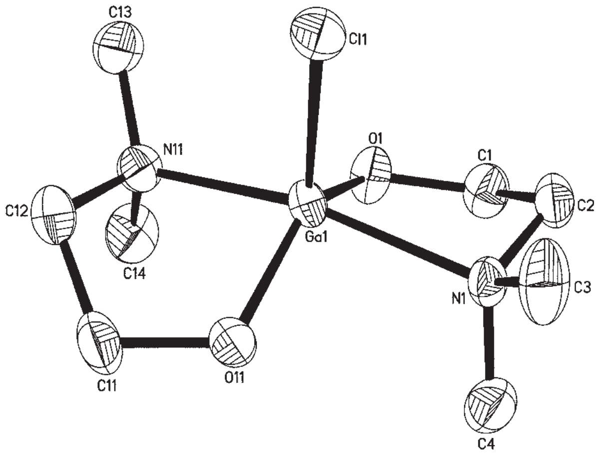

Fig. 1 Crystal structure showing the major component of $[Ga(OCH_2CH_2NMe_2)_2Cl]$ (**6**) with thermal ellipsoids drawn at the 50% probability level (hydrogen atoms omitted for clarity).

Table 1 Selected bond lengths (Å) and angles (°) for compounds **6** and **7**

Bond lengths/angles[a]	Compound **6**	Compound **7**
Ga1–O1	1.841(2)	1.8373(12)
Ga1–O11	1.842(3)	1.8389(12)
Ga1–N1	2.161(3)	2.1516(15)
Ga1–N11	2.118(3)	2.1681(15)
Ga1–Cl1	2.2433(8)	2.2094(5)
O1–Ga1–O11	135.08(13)	118.91(6)
O1–Ga1–N1	83.45(11)	84.28(6)
O1–Ga1–N11	91.27(11)	89.82(6)
O1–Ga1–Cl1	114.18(9)	121.55(4)
O11–Ga1–N1	89.37(12)	90.34(6)
O11–Ga1–N11	84.89(12)	84.18(5)
O11–Ga1–Cl1	110.70(10)	119.54(4)
N1–Ga1–Cl1	97.05(7)	95.45(4)
N11–Ga1–Cl1	97.38(8)	95.76(4)
N1–Ga1–N11	165.55(11)	168.80(6)

[a] Only the values for the major component of **6** are given. Symmetry code: (i) −*x*, −*y*, −*z* + 1.

crystallised into the triclinic space group $P\bar{1}$ shown in Fig. 2. The gallium atom in **7** adopts a distorted trigonal bipyramidal geometry as observed for **6**, with the oxygen atoms of each alkoxide and a chlorine atom occupying the three equatorial positions and the N atoms of the NMe_2 group in the axial positions. The Ga–N (av. 2.160 Å) and Ga–O (av. 1.838 Å) bond distances are similar to those observed in **6**.

The crystal structure of compound **8** was determined by single crystal X-ray diffraction, the results are shown in Fig. 3; selected bond lengths and angles are given in Table 2. Compound **8** crystallised into the monoclinic space group $P2_1/n$. As shown in Fig. 3, the compound exhibits a dimeric molecular arrangement. The centrosymmetric, four-membered Ga_2O_2 ring is planar, and each gallium atom is coordinated in a distorted trigonal bipyramidal geometry with two chlorine atoms in equatorial positions. The bridging alkoxide substituents are located in both axial and equatorial positions, while the donor atom (O) of the alkoxide ligand is in the other axial position. The equatorial Ga1–O2 (1.886(2) Å) bond length is significantly shorter than the axial one Ga1–O2^{i} (1.9753(17) Å). As expected, the Ga1–OMe dative bond distance (2.1613(19) Å) is the longest Ga–O bond. The O2^{i}–Ga1–O1 bond angle to the opposite, axial alkoxide group is 154.27(8)°. This large deviation from 180° is due to the constraints of the internal O2^{i}–Ga1–O2 angle of 76.30(9)° in the Ga_2O_2 ring and the geometry of the ligand. Similar distorted trigonal bipyramidal geometry at the metal centre has been noted in the closely related intramolecularly stabilised diorganoalkoxometallanes, of the type $[Me_2MOR]_2$ (R = $OCH_2CH_2NMe_2$, OCH_2CH_2OMe, $OCH(CH_3)CH_2NMe_2$ and $OCH(CH_3)CH_2OMe$).[11,13,16–18] These structures are also dimeric in the solid state and consist of planar, or nearly planar, M_2O_2 rings. The metal centres are also coordinated in distorted trigonal bipyramidal geometry with comparable bond lengths and angles.

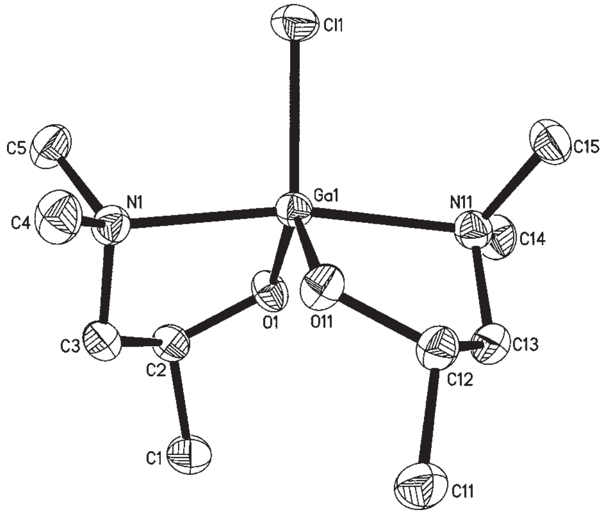

Fig. 2 Crystal structure of $[Ga(OCH(CH_3)CH_2NMe_2)_2Cl]$ (**7**) with thermal ellipsoids shown at the 50% probability level (hydrogen atoms omitted for clarity).

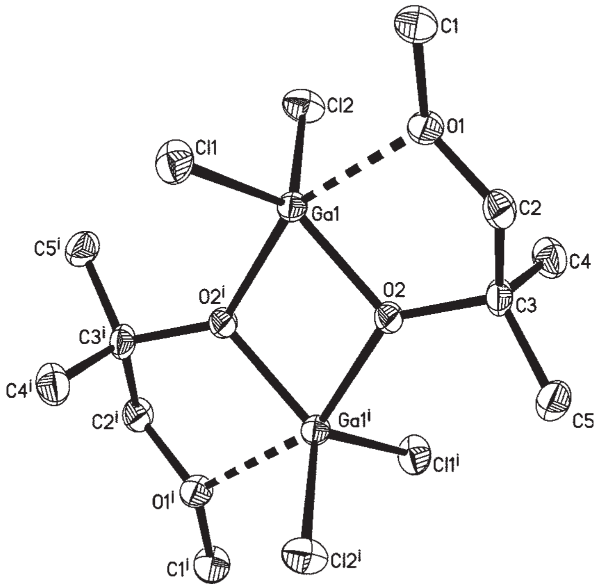

Fig. 3 X-Ray structure of $[Ga(OC(CH_3)_2CH_2OMe)Cl_2]_2$ (**8**) with thermal ellipsoids shown at the 50% probability level (hydrogen atoms omitted for clarity). Symmetry code: (i) −*x*, −*y*, −*z* + 1.

Table 2 Selected bond lengths (Å) and angles (°) for compound **8**

Bond lengths/Å			
Ga1–O1	2.1613(19)	Ga1–O2	1.886(2)
Ga1–O2^{i}	1.9753(17)	Ga1–Cl1	2.1715(8)
Ga1–Cl2	2.1595(8)		
Bond angles/°			
O1–Ga1–O2	77.98(7)	O2–Ga1–O2^{i}	76.30(9)
O2–Ga1–Cl2	120.54(7)	O2^{i}–Ga1–Cl2	102.35(6)
O1–Ga1–Cl2	91.29(6)	O2^{i}–Ga1–O1	154.27(8)
O2^{i}–Ga1–Cl1	100.69(6)	O2–Ga1–Cl1	122.49(7)
O1–Ga1–Cl1	92.44(5)	Cl2–Ga1–Cl1	116.19(3)

Symmetry code: (i) −*x*, −*y*, −*z* + 1.

Conclusions

The reaction of $[Ga(NMe_2)_nCl_{3-n}]$ (n = 1–3) with donor functionalised alcohols resulted in the formation of a range of gallium alkoxides. Thus, reaction of $[Ga(NMe_2)_3]_2$ with excess ROH (R = $CH_2CH_2NMe_2$, $CH(CH_3)CH_2NMe_2$, $C(CH_3)_2CH_2OMe$, CH_2CH_2OMe) in hexane at room temperature afforded colourless oils of the homoleptic gallium tris(alkoxides) $[Ga(OR)_3]_2$. The side-products $[Ga(OCH_2CH_2NMe_2)_2Cl]$, $[Ga(OCH(CH_3)CH_2NMe_2)_2Cl]$ and $[Ga(OC(CH_3)_2CH_2OMe)Cl_2]_2$ were also isolated in low yield during the synthesis. Direct synthesis of the novel gallium bis(alkoxides) was achieved from the reaction of $[Ga(NMe_2)_2Cl]$ and two equivalents of ROH (R = $CH_2CH_2NMe_2$, $CH(CH_3)CH_2NMe_2$). The gallium mono(alkoxide), $[Ga(OC(CH_3)_2CH_2OMe)Cl_2]_2$, was synthesized from the reaction of $[Ga(NMe_2)Cl_2]$ and $HOC(CH_3)_2CH_2OMe$. X-Ray crystallography showed that the gallium bis(alkoxide)s (**6** and **7**) are monomeric in the solid state, whereas the gallium mono(alkoxide) **8** is dimeric.

Experimental

General procedures

All manipulations were performed under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in an Mbraun Unilab glovebox. All solvents used were stored in alumina columns and dried with anhydrous engineering equipment, such that the water concentration was 5–10 ppm. The gallium amides, $[Ga(NMe_2)_3]_2$ (**1**), $[ClGa(NMe_2)_2]$ (**9**) and $[Cl_2Ga(NMe_2)]$ (**10**) were prepared according to literature procedures and compounds **2** and **3** *via* modified literature routes.[3,14,19] All other reagents were procured commercially from Aldrich and the alcohols were degassed by three freeze–pump–thaw cycles and stored over 4 Å molecular sieves. Microanalytical data were obtained at UCL. All ^1H and ^{13}C NMR spectra were obtained on a Bruker AMX400 spectrometer, operating at 400.12 MHz. All spectra were recorded using CD_2Cl_2, which was dried and degassed over molecular sieves prior to use or C_6D_6 which was dried using Na/benzophenone; ^1H and ^{13}C chemical shifts are reported relative to $SiMe_4$ (δ 0.00). All IR spectra were recorded using a Shimadzu FTIR-8200 spectrometer, operating in the region of 4000–400 cm^{-1}. The IR samples were prepared using Nujol. The mass spectra were obtained using a Micromass 70-SE spectrometer using Chemical Ionization (CI) with methane reagent gas.

1: Anal. Calc. (%) for $C_{12}H_{36}N_6Ga_2$: C, 35.68; H, 8.97, 20.81. Found (%): C, 35.17; H, 8.97; N, 20.14. ^1H NMR (CD_2Cl_2): δ/ppm 2.69 (s, μ-NCH_3, 12H), 2.68 (s, NCH_3, 24H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ/ppm 42.9 (NCH_3), 43.2 (μ-NCH_3). IR (cm^{-1}): 2814 s, 2767 s, 1463 s, 1259 s, 1128 m, 1040 w, 899 *vs*., 502 *vs*.

Synthesis of 2. $HOCH_2CH_2NMe_2$ (0.8 mL, 7.96 mmol) was added dropwise to a solution of $[Ga(NMe_2)_3]_2$ (0.5 g, 1.24 mmol) in hexane (20 mL) at −78 °C with stirring over a 0.5 h period. The reaction mixture was allowed to warm slowly to room temperature and stirred for 24 h. Removal of the solvent *in vacuo* afforded a clear oil (0.58 g, yield 70%). ^1H NMR δ/ppm (CD_2Cl_2): 2.12 (s, NCH_3, 36H), 2.29 (t, OCH_2CH_2N, 12H, J = 8.1 Hz), 3.55 (t, OCH_2CH_2N, 12H, J = 8.1 Hz). $^{13}C\{^1H\}$NMR δ/ppm (CD_2Cl_2): 45.0 (NCH_3), 59.2 (OCH_2CH_2N), 61.6 (OCH_2CH_2N). IR (cm^{-1}): 3256 *vs*., 2913 *vs*., 2191 s, 1974 *vs*., 1812 s, 1678 s, 1605 m, 1454 *vs*., 1405 s, 1368 s, 1350 s, 1327 m, 1272 s, 1185 m, 1156 m, 1084 s, 949 s, 887 s, 787 s, 731 s, 696 m, 623 *vs*., 561 s. Mass Spec (CI): (m/z) 580 ([M] − $OCH_2CH_2NMe_2$), 334 $Ga(OCH_2CH_2NMe_2)_3$, 245 $Ga(OCH_2CH_2NMe_2)_2$, 158 $Ga(OCH_2CH_2\ NMe_2)$.

Synthesis of 3. Compound **3** was prepared in the same manner as to **2** using $HOCH(CH_3)CH_2NMe_2$ (1.0 mL, 8.11 mmol), $[Ga(NMe_2)_3]_2$ (0.5 g, 1.24 mmol) and hexane (20 mL). Removal of the solvent *in vacuo* afforded a yellow non-viscous oil (0.54 g, yield 58%). ^1H NMR δ/ppm (CD_2Cl_2): 1.09 (d, $OCH(CH_3)$, 18H, J = 5.8 Hz), 2.21–2.11 (broad, $OCHCH_2N$, 12H), 2.31 (broad, NCH_3, 36H), 3.86 (m, $OCH(CH_3)CH_2$, 6H). $^{13}C\{^1H\}$NMR δ/ppm (CD_2Cl_2): 24.1 ($GaOCH(CH_3)$), 46.4 (NCH_3), 63.4 ($OCHCH_2N$), 69.4 ($GaOCH$). IR (cm^{-1}): 2924 s, 2361 m, 2342 m, 1457 *vs*., 1377 m, 1347 v, 1322 m, 1260 s, 1188 m, 1137 s, 1092 s, 1030 m, 1012 s, 955 s, 858 m, 836 m, 802 w, 722 s, 668 m, 637 s, 539 w, 496 m, 479 s. Mass Spec (CI): (m/z) 752 [M], 376 $Ga(OCH(CH_3)CH_2NMe_2)_3$ 273 $Ga(OCH(CH_3)CH_2NMe_2)_2$ 102 $(OCH(CH_3)CH_2NMe_2)$, 86 $CH(CH_3)CH_2NMe_2$, 58 (CH_2NMe_2).

Synthesis of 4. Compound **4** was prepared in the same manner as **2** but using $HOC(CH_3)_2CH_2OMe$ (1.00 mL, 8.56 mmol), $[Ga(NMe_2)_3]_2$ (0.5 g, 1.24 mmol) in hexane (20 mL). Removal of the solvent *in vacuo* afforded a brown non-viscous oil (0.56 g, yield 60%). ^1H NMR δ/ppm (C_6D_6): 1.11 (s, $OC(CH_3)$, 36H), 2.89 (s, $GaOCCH_2$, 12H), 2.96 (s, OCH_3, 18H). $^{13}C\{^1H\}$ NMR δ/ppm (C_6D_6): 26.3 ($OC(CH_3)$), 58.8 (OCH_3), 69.7 ($OCCH_2$), 81.4 ($OCCH_2$). IR (cm^{-1}): 2962 m, 2360 m, 1614 w, 1455 m, 1384 m, 1261 m, 1092 s, 1020 s, 799 s, 666 m. Mass Spec (CI): (m/z) 655 [M] − $OC(CH_3)_2CH_2OCH_3$, 379 [M], 275 $Ga(OC(CH_3)_2CH_2OCH_3)_2$, 87 $(C(CH_3)_2CH_2OCH_3)$.

Synthesis of 5. Compound **5** was prepare in the same manner as **2** using $HOCH_2CH_2OMe$ (0.6 mL, 7.61 mmol) and $[Ga(NMe_2)_3]_2$ (0.5 g, 1.24 mmol) in hexane (20 mL). Removal of the solvent *in vacuo* afforded a yellow non-viscous oil (0.38 g, yield 52%). ^1H NMR δ/ppm (C_6D_6): 3.23 (s, OCH_3, 18H), 3.43 (b, $OCH_2CH_2OCH_3$, 12H), 4.19 (t, $OCH_2CH_2OCH_3$, 12H). $^{13}C\{^1H\}$NMR δ/ppm (C_6D_6): 58.6 (OCH_3), 63.1 ($OCH_2CH_2OCH_3$), 72.6 ($OCH_2CH_2OCH_3$). IR (cm^{-1}): 2880 s, 2714 s, 2396 s, 2153 s, 1971 *vs*., 1606 s, 1455 *vs*., 1396 s, 1365 s, 1331 s, 1241 s, 1199 s, 1092 s, 964 s, 904 s, 842 s, 700 s, 733 s, 697 s. Mass spec. (CI): (m/z) 589 [M], 515 [M] − OCH_2CH_2OMe, 19 $Ga(OCH_2CH_2OMe)_2$.

Synthesis of 6. $HOCH_2CH_2NMe_2$ (0.75 mL, 7.37 mmol) was added dropwise to a solution of **9** (0.7126 g, 3.69 mmol) in hexane (20 mL) at −78 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred for 24 h. Removal of the solvent *in vacuo* afforded a pale yellow solid (0.6203 g, yield 60%). ^1H NMR δ/ppm (C_6D_6): 2.00 (NCH_3, 18H), 2.27 (t, OCH_2CH_2N, 6H, J = 5.4 Hz), 3.93 (t, OCH_2CH_2N, 6H, J = 5.4 Hz). $^{13}C\{^1H\}$ NMR δ/ppm (C_6D_6): 43.9 (NCH_3), 58.7 (OCH_2CH_2N), 60.4 (OCH_2CH_2N). Mass spec. (CI): (m/z) 281 [M], 246 [M] − Cl, 194 [M] − $OCH_2CH_2NMe_2$, 158 $[Ga(OCH_2CH_2NMe_2)]$, 88 $[OCH_2CH_2NMe_2]$. Anal. Calc. for

Table 3 Crystallographic data summary for compounds **6**, **7** and **8**

	6	**7**	**8**
Formula	$C_8H_{20}ClGaN_2O_2$	$C_{10}H_{22}ClGaN_2O_2$	$C_{10}H_{22}Cl_4Ga_2O_4$
Formula weight	281.43	309.48	487.52
T/K	150(2)	150(2)	150(2)
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	$Pna2_1$	$P\bar{1}$	$P2_1/n$
a/Å	9.3818(8)	7.7913(13)	8.4505(10)
b/Å	12.2919(10)	7.9556(13)	13.7024(17)
c/Å	10.7257(9)	12.052(2)	8.6396(11)
α/°	90	99.069(2)	90
β/°	90	93.211(3)	113.648(2)
γ/°	90	102.462(2)	90
V/Å^3	1236.89(18)	717.2(2)	916.4(2)
Z	4	2	2
D_c/g cm^{-3}	1.511	1.433	1.767
μ(Mo Kα)/mm^{-1}	2.421	2.095	3.529
Reflns collected	10360	6168	13241
Indep reflns (R_{int})	2945 (0.0220)	3265 (0.0156)	4429 (N/A)
$R1$ [$F^2 > 2\sigma$]	0.0273	0.0264	0.0294
$wR2$ (all data)	0.0637	0.0662	0.0829

$C_8H_{20}ClGaN_2O_2$: C, 34.14; H, 7.16; N, 9.95%. Found: C, 34.66; H, 7.72; N, 9.05%.

Synthesis of 7. $HOCH(CH_3)CH_2NMe_2$ (1.1 mL, 8.30 mmol) was added dropwise to a stirred solution of **9** (0.8023 g, 4.15 mmol) in hexane (20 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. Removal of the solvent *in vacuo* afforded a white crystalline solid (0.6923 g, yield 54%). ^1H NMR δ/ppm (CD_2Cl_2): 1.31 (d, $OCH(CH_3)$, 6H, J = 5.8 Hz), 2.29–2.41 (broad, $OCHCH_2N$, 4H), 2.49 (broad, NCH_3, 12H), 3.95 (m, $OCH(CH_3)CH_2$, 2H). Mass spec. (CI): (m/z) 309 [M], 273 [M] − Cl, 206 [M] − $OCH(CH_3)CH_2NMe_2$, 102 [$OCH(CH_3)CH_2NMe_2$], 86 $OCH(CH_3)CH_2NMe_2$. Anal. Calc. for $C_{10}H_{24}ClGaN_2O_2$: C, 38.81; H, 7.81; N, 9.05%. Found: C, 38.88; H, 7.08; N, 9.67%.

Synthesis of 8. $HOC(CH_3)_2CH_2OMe$ (0.4 mL, 3.26 mmol) was added dropwise to a stirred solution of **10** (0.6027 g, 3.26 mmol) in hexane (20 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 24 h. Removal of the solvent *in vacuo* afforded a white crystalline solid (0.4936 g, yield 62%). ^1H NMR δ/ppm (CD_2Cl_2): 1.48 (s, $OC(CH_3)$, 12H), 2.58 (s, $GaOCCH_2$, 4H), 3.60 (s, OCH_3, 6H). $^{13}C\{^1H\}$ NMR δ/ppm (C_6D_6): 26.1 ($OC(CH_3)$), 58.9 (OCH_3), 70.1 ($OCCH_2$), 79.9 ($OCCH_2$). Mass spec. (CI): (m/z) 451 [$Ga(OC(CH_3)_2CH_2OMe)_3Cl_2$], 290 [$Ga(OC(CH_3)_2CH_2OMe)_2Cl_2$–$OC(CH_3)_2CH_2OMe$], 245 [$Ga(OC(CH_3)CH_2OMe)_2Cl_2$], 87 [$C(CH_3)_2CH_2OMe$]. Anal. Calc. for $C_5H_{11}Cl_2GaO_2$: C, 24.64; H, 4.55%. Found: C, 25.02; H, 4.26%.

X-Ray crystal structures determination

Crystals of **6–8** were obtained from oils at room temperature after a few days. A single crystal was mounted on a glass fibre and all geometric and intensity data were taken from this sample on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 150 ± 2 K. Data reduction and integration was carried out with SAINT+[20] and absorption corrections applied using the program SADABS[21] (**6**, **7**). All of the structures were solved by direct methods using SHELXS-97[22] and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis.[23] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and their thermal parameters linked to those of the atoms to which they were attached (riding model). Crystallographic refinement parameters of complexes **6** to **8** are summarized in Table 3, and the selected bond distances and angles of these complexes are listed in Tables 1 and 2.

The structure of [$Ga(OCH_2CH_2NMe_2)_2Cl$] (**6**) was found to have both enantiomeric forms on the same site with the ratio 82 : 18 and with Ga1 and Cl1 common to both. The ligands were modelled anisotropically with suitable constraints and restraints. Also, the structure was refined as a racemic twin with the ratio 66 : 33.

The structure of [$Ga(OC(CH_3)_2CH_2OMe)Cl_2]_2$ (**8**) was found to be a non-merohedral twin so GEMINI[24] was used to index the data which showed that there were two, approximately equal components. The output p4p files for each component were read back into SMART[25] and run through the BRAVAIS and L.S. routines. The data were combined to give a single p4p file and integrated simultaneously using SAINT+.[20] The twin law was found to be 0.04 0 0.96/0 −1 0/1.04 0 0.04. The dataset had 5280 data from component 1 only, 5271 data from component 2 only and 2690 data belonging to both. I/σ for overlapping reflections was 28.4. The dataset was corrected for absorption using TWINABS[26] which was also used to produce an HKLF 4 file (non-overlapping reflections for component 1 only) for structure solution and initial refinement and an HKLF 5 file for final refinement of the structure. The twin ratio refined to 0.4392(15) (using the BASF instruction).

All of the structure diagrams were produced using the SHELXTL program suite.[27]†

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