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Review

Gallium(III) and indium(III) alkoxides and aryloxides

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Contents

Abstract

This article presents a systematic and extensive review of the syntheses, structures and reactivities of gallium(III) and indium(III) alkoxides and aryloxides. Mono-, bis- and tris(alkoxides) and (aryloxides) have been synthesised and structurally characterised for both gallium(III) and indium(III) and the applications of these compounds are also discussed.

Keywords: Gallium(III) alkoxide; Indium(III) alkoxide; Synthesis

1. Introduction

A large number of alkylgallium(III) alkoxides $[R_{3-x}Ga(OR')_x]_n$ ($x = 1$ and 2) and homoleptic gallium(III) alkoxides $[Ga(OR')_3]_n$ have been reported. In contrast, until recently, there were few reports on the chemistry of indium(III) alkoxides. Group 13 alkoxides have been used extensively in organic reactions. For example, intramolecularly donor-stabilised gallium alkoxides are used as alkylating reagents in the cross-coupling of aryl-triflates and aryl-halides [1,2]. Homoleptic gallium alkoxides are also intermediates to heterometallic complexes $[ZnGa_2(OR)_8]_n$, which serve as precursors to $ZnGa_2O_4$ materials [3]. In addition, gallium alkoxides have been employed as precursors to Ga_2O_3 films via low-pressure chemical vapour deposition (LPCVD) [4–6]. High-quality indium oxide has also been produced by LPCVD of indium alkoxides [7].

The majority of the known alkoxide complexes of gallium and indium are of the type $[R_2M–OR']$ and feature a 1:1 stoichiometry. These complexes are characterised by a

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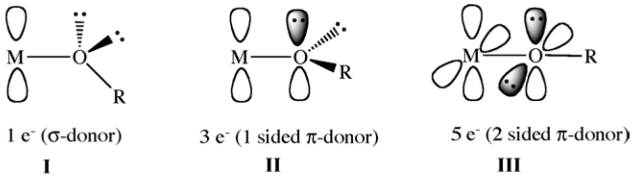


Scheme 1.

marked tendency to oligomerise through the formation of strong metal–oxygen bridges. Monomeric alkoxide derivatives can be stabilised by the presence of bulky substituents on the group 13 and oxygen atoms. Alkoxide ligands are generally classified as 'hard' and thus show a strong preference to form bonds with 'hard' metal centres in higher oxidation states. Alkoxide ligands can act as 1-electron σ-donors, or as 3- or 5-electron π-donor ligands via overlap with appropriate metal orbitals of π-symmetry, according to Scheme 1.

Bonding of the alkoxide ligand as a two-sided π-donor has never been observed in gallium alkoxides since this bonding mode requires sp hybridisation at both Ga and O centres, which is highly energetically unfavourable. Alkoxide ligands could act as one-sided π-donors to gallium centres given the preference of Ga to adopt sp^2 hybridisation and the ability of O valence s- and p-orbitals to rehybridise easily. However, studies have shown that π-bonding contributions in gallium alkoxide compounds are small due to the large size difference between Ga and O and the polar character of these bonds, as discussed in a number of reviews [8a,b].

Recently, there has been a discernible shift in interest towards the heavier elements in group 13 and this review will concentrate on gallium(III) and indium(III) alkoxide complexes. Aluminium organoalkoxides have been described in a number of reviews [9]. Previous reviews [8,10] have covered some aspects of alkoxide chemistry of gallium and indium, however there has been considerable recent activity in this field and thus, an up-to-date review was needed. Structural data (M–O bond lengths, O–M–O and M–O–M bond angles) for selected examples of gallium(III) and indium(III) alkoxide/aryloxide complexes are presented in Table 1. The chemistry of heterometallic alkoxides incorporating group 13 elements has been reviewed extensively and will not be covered in this review [11]. In addition, the synthesis and characterisation of group 13 sesquialkoxides has been recently reviewed and will only be mentioned briefly [9b,12].

The following abbreviations will be used—Ac: acetate (CH_3CO_2); BINOL: 2,2′-dihydroxy-1,1′-binapthyl; bz: benzyl (CH_2Ph); Cp: cyclopentadienyl; Cy: cyclohexyl; Dipp: 2,6-diisopropylphenyl ($-C_6H_3$-2,6-^{i}Pr$_2$); Haloz: 2-(2′-hydroxy-3′-allylphenyl)-2-oxazoline; Hbroz: 2-(5′-bromo-2′-hydroxyphenyl)-2-oxazoline; Hhbo: 2-(2′-hydroxyphenyl)-2-benzoxazole; Hima: isomaltol; Hmoz: 2-(2′-hydroxy-3′-methylphenyl)-2-oxazoline; Hoz: 2-(2′-hydroxyphenyl)-2-oxazoline; mim: *N*-methylimidazol-2-yl; Np: naphthyl; py: pyridine; pyz: pyrazine ($N_2C_4H_4$); quin: quinoline; thf: tetrahydrofuran; tmp: 2,2,6,6-tetramethylpiperinato.

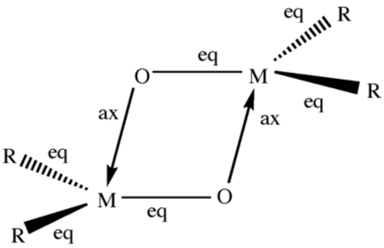


Fig. 1. Representation of the formation of the M_2O_2 ring in mono(alkoxides).

2. Mono(alkoxides) and (aryloxides)

Various methods have been used to synthesise mono (alkoxides) of gallium(III) and indium(III), the most common being the reaction of trivalent gallium or indium organometallics [R_3M] with alcohols at elevated temperatures, according to Eq. (1).

$$R_3M + R'OH \rightarrow \tfrac{1}{n}[R_2MOR']_n + RH \qquad (1)$$

Salt elimination routes have also been employed for the synthesis of gallium and indium mono(alkoxides) via the reaction of organometallic halide complexes [R_2MX] (R = alkyl or aryl, M = Ga or In, X = halide) with early main group reagents (e.g. LiOR′, for example, Eq. (2)). An alternative route to mono(alkoxide) complexes involves amine–alcohol exchange, as shown in Eq. (3).

$$R_2MX + LiOR' \rightarrow \tfrac{1}{n}[R_2MOR']_n + LiX \qquad (2)$$

$$[R_2M(NR'_2)]_n + R'OH \rightarrow \tfrac{1}{n}[R_2MOR']_n + HNR'_2 \qquad (3)$$

Mono(alkoxides) of the type $[R_2MOR']_n$ (R = akyl or aryl; M = Ga or In; R′ = alkyl, aryl) have been structurally characterised for both gallium(III) and indium(III), as discussed in detail below. The structure of these compounds is governed by electronic and steric properties of both the alkoxide and alkyl/aryl ligands. In general, gallium and indium alkoxides are either monomeric or dimeric via alkoxy bridges. The dimers are derived from two sp^2 hybridised M atoms, which are then bridged by two alkoxide ligands forming a M_2O_2 ring, according to Fig. 1. Thus, one alkoxide ligand forms an M–O σ-bond and lies within the equatorial plane of M. The other alkoxide ligand forms a dative covalent M–O bond via electron pair donation from O into a vacant p-orbital on M and lies axial to the M centre. The situation is reversed for the second M and each alkoxide ligand is sp^3 hybridised at O. These complexes are generally air/moisture sensitive compounds and highly soluble in a range of organic solvents.

2.1. Gallium(III)

Over 50 years ago dimethylgallium methoxide [$Me_2Ga(OMe)]_3$ (**1**) was reported [13]. Compound **1** was prepared from the reaction of Me_3Ga and methanol, according to Eq. (1). A series of related complexes $[Me_2Ga(OR')]_n$ (R′ = CH_3,

Table 1
Selected bond lengths and angles for gallium and indium alkoxides and aryloxides

No.	Compound	Framework	M—O$_{\mathrm{alkoxide}}$ bond length (Å)	O—M—O bond angle (°)	M—O—M bond angle (°)	Reference
Gallium mono(alkoxides)/(aryloxides)						
3	[^{t}Bu$_2$Ga(O^{t}Bu)]$_2$	Ga$_2$O$_2$ ring, planar	1.990(2)	76.1(1)	103.9(1)	[16]
4	[Me$_2$Ga(OCy)]$_2$	Ga$_2$O$_2$ ring, planar	1.954(4)	80.2(2)	99.8(2)	[21]
11	[^{t}Bu$_2$Ga(OMe)]$_2$	Ga$_2$O$_2$ ring, folded	1.955(3)	76.5(1)	103.5(1)	[22]
13	[^{t}Bu$_2$Ga(O^{n}Pr)]$_2$	Ga$_2$O$_2$ ring, planar	1.947(7) 1.958(5)	76.5(3)	103.5(3)	[22]
18	[^{t}Bu$_2$Ga(O^{n}C$_5$H$_{11}$)]$_2$	Ga$_2$O$_2$ ring, planar	1.969(7) 1.948(7)	76.5(3)	103.1(2)	[22]
20	[^{t}Bu$_2$Ga(OCHEt$_2$)]$_2$	Ga$_2$O$_2$ ring, planar	1.956(3)	76.5(1)	103.5(1)	[22]
21	[^{t}Bu$_2$Ga(OCH$_2$^{t}Bu)]$_2$	Ga$_2$O$_2$ ring, planar	1.984(2)	78.3(1)	101.7(1)	[22]
22	[^{t}Bu$_2$Ga(O^{n}C$_6$H$_{13}$)]$_2$	Ga$_2$O$_2$ring, folded	1.91(1) 1.97(1)	76.8(4)	103.2(4)	[22]
24	[^{t}Bu$_2$Ga(OPh)]$_2$	Ga$_2$O$_2$ ring, planar	2.035(1)	78.3(1)	101.7(1)	[23]
26	[^{t}Bu$_2$Ga(OCH(CF$_3$)$_2$)]$_2$	Ga$_2$O$_2$ ring, planar	2.02(2) 2.10(2)	73.9(9) 77.0(9)	104.5(4)	[23]
27	[^{t}Bu$_2$Ga(OCPh$_3$)]	R$_2$GaO core, distorted trigonal planar	1.831(4)			[24]
28	[^{t}Bu$_2$Ga(OC$_6$H$_4$-2,4-^{t}Bu$_2$-4-Me)]	R$_2$GaO core, distorted trigonal planar	1.821(3)			[25]
35	[(PhCH$_2$)$_2$Ga(OCH$_2$Ph)]$_2$	Ga$_2$O$_2$ ring, planar	1.951(2)	79.9(1)	100.1(1)	[29]
36	[(η^1-Cp)$_2$Ga(OEt)]$_2$	Ga$_2$O$_2$ ring, planar	1.940(3) 1.906(3)	79.5(2)	100.5(2)	[31]
37	[{(Me$_3$Si)CH$_2$}$_2$Ga(OCH$_2$(SiMe$_3$)]	Ga$_2$O$_2$ ring, planar	1.967(4) (av.)	81.6(1)	98.4(1)	[32]
38	[{(Me$_3$Si)$_2$CH}$_2$Ga(OC$_6$F$_5$)]	R$_2$GaO core, planar	1.843			[33]
42	[H$_2$Ga(O^{t}Bu]$_2$	Ga$_2$O$_2$ ring, planar	1.908(9) 1.902(9)	78.6(5)	101.4(5)	[36]
43	[H$_2$Ga(OCH^{t}Bu$_2$)]$_2$	Ga$_2$O$_2$ ring, planar	1.93(1)		99.3(3)	[37]
49	[Me$_2$Ga(OCH$_2$CH$_2$NMe$_2$)]$_2$	Ga$_2$O$_2$ ring, planar	1.913(3) 2.078(3)	74.6(1)	105.4(1)	[41]
50	[H$_2$Ga(OCH$_2$CH$_2$NMe$_2$)]$_2$	Ga$_2$O$_2$ ring, planar	1.911(3) 2.053(3)	74.7(1)	105.3	[41]
51	[Me$_2$Ga(OCH(CH$_3$)CH$_2$NMe$_2$)]$_2$	Ga$_2$O$_2$ ring, nearly planar	1.919(2) 2.097(2)	76.2(1)	103.1	[42]
53	[Me$_2$Ga(OCH$_2$CH$_2$OMe)]$_2$	Ga$_2$O$_2$ ring, planar	1.934(6) 2.012(7)	75.46(8)	101.5(3)	[44]
54	[Me$_2$Ga(OCH(CH$_3$)CH$_2$OMe)]$_2$	Ga$_2$O$_2$ ring, planar	1.914(4) 1.999(4)	78.0(2)	102.0(2)	[44]
57	[Me$_2$Ga(OCH$_2$CH(^{i}Pr)NMe$_2$)]$_2$	Ga$_2$O$_2$ ring	1.904(2) 1.917(2) 2.070(2) 2.075(2)	73.01(9) 73.39(10)	104.80(11)	[45]

59	$[Me_2Ga(OCH_2CH(Bz)NMe_2)]_2$	Ga_2O_2 ring	1.908(3) 1.916(3) 2.075(3) 2.098(4)	72.34(14) 71.66(14)	103.0(2)	[45]
60	$[Me_2Ga(OCH_2CH(Et)NMe_2)]_2$	Ga_2O_2 ring	1.905(8) 1.913(7) 2.080(7) 2.097(8)	73.0(3) 73.5(3)	103.8(3)	[45]
61	$[Me_2Ga(OCH(Ph)CH(CH_3)NHMe)]_2$	Ga_2O_2 ring, planar	1.922(3) 2.088(3)	73.70(4)	106.18(4)	[46]
71	$[Me_2Ga(OC_6H_4\text{-}2\text{-}OMe)]_2$	Ga_2O_2 ring, planar	1.957(4) 2.046(4)	75.6(2)	104.4(2)	[42]
75	$[Me_2Ga(OCH(Me)C_6H_4\text{-}2\text{-}OMe)]_2$	Ga_2O_2 ring, planar	1.951(2) 1.957(2)	80.7(1)	99.2(1)	[44]
76	$[Me_2Ga(OCPh)(CH_2Ph)CH(CH_3)\text{-}CH_2NMe_2)]$	R_2GaON core, tetrahedral	1.846(2)			[52]
77	$[Me_2Ga(OCH(Ph)CH(CH_3)NMe_2)]_2$	Ga_2O_2 ring, planar	1.911(3) 2.128(3)	71.6(1)	103.1(1)	[52]
81	$[Me_2Ga(OC(CF_3)_2CH_2NMe_2)]$	R_2GaON core, tetrahedral	1.890(2)			[54]
91	$[Me_2Ga(Oquin)]_2$	Ga_2O_2 ring, planar	1.937(3) 2.297(3)	71.3(1)	108.7(1)	[61]
92	$[(C_5H_9)_2Ga(Oquin)]_2$	Ga_2O_2 ring, slightly folded	1.941 2.342	70.6(2) 71.3(2)	108.7(2) 109.4(2)	[62]
96	$[Me_2Ga(OCH_2CH_2NH_2)]$	R_2GaON core, tetrahedral	1.916(5) 1.917(4)			[65]
97	$[Me_2Ga(OCH_2CH_2CH_2NH_2)]$	R_2GaON core, tetrahedral	1.879 (av.)			[66]
98	$[Me_2Ga(OCH_2CH(CH_3)NH_2)]_2$	Ga_2O_2 ring, planar	1.923 (av.)	75.1(4)	105.37(17)	[66]
Indium mono(alkoxides)/(aryloxides)						
115	$[^tBu_2In(OEt)]_2$	In_2O_2 ring, planar	2.165(5) 2.14(5)	75.2(2)	104.8(2)	[80]
116	$[^tBu_2In(OMe)]_2$	In_2O_2 ring, planar	2.153(2)	75.2(1)	104.8(1)	[81]
117	$[Me(Cl)InO^tBu]_2$	In_2O_2 ring, planar	2.115(7) (av.)	77.0(2)	103.0(1)	[82]
118	$[Me(Br)InO^tBu]_2$	In_2O_2 ring, planar	2.121(7) (av.)	77.0(3)	103.0(3)	[82]
119	$[\{(Me_3Si)_2N\}MeInO^tBu]_2$	In_2O_2 ring, planar	2.145(7) (av.)	75.0(1)	105.0(1)	[82]
120	$[Me(Cl)InOC_6H_4\text{-}2\text{-}OMe]_2$	In_2O_2 ring, planar	2.204(4) (av.)	72.4(2)	107.5(2)	[82]
121	$[Me_2In(OC_6H_4CHO)]_2$	In_2O_2 ring, planar	2.286(3)	74.8(1)		[83]
123	$[(\eta^1\text{-}Cp)_2In(O^tBu)]_2$	In_2O_2 ring, planar	2.118(2) 2.141(2)	75.03(6)	104.97(6)	[85]
128	$[Me_2In(OC(CF_3)_2CH_2NH(CH_2)_2OMe)]_2$	In_2O_2 ring, nearly planar	2.2034(8) 2.3959(8)	73.81(3)	106.19(3)	[88]

Table 1 (*Continued*)

No.	Compound	Framework	M—O$_{alkoxide}$ bond length (Å)	O—M—O bond angle (°)	M—O—M bond angle (°)	Reference
133	$[Me_2In(OCH_2CH_2(2\text{-}C_5H_4N)]_2$	In_2O_2 ring, planar	2.132(5) 2.240(5)	75.4(2)	104.6(2)	[59]
135	$[MeIn(OC(Ph)(py)_2]NO_3$	In_2O_2 ring, slightly folded	2.208(6) 2.165(6) 2.422(12)	73.2(3) 82.1(3) 83.3(3)	105.9(3) 107.2(2)	[90]
138	$[MeIn(OC(mim)_2(py)]NO_3$	In_2O_2 ring, slightly folded	2.205(6)–2.299(6)	70.5(2)	118.2(3)	[90]
140	$[In(\kappa^4\text{-}L^b)Cl_2]$	N_3OInCl_2 core, octahedral	2.076(5)			[67]
Gallium bis(alkoxides)/(aryloxides)						
148	$[HGa(O^tBu)_2]_2$	Ga_2O_2 ring	1.783(4)[a] 1.906(4)[b]	106.9(2)[c]	100.6(2)	[36]
149	$[(THF)MeGa((S)\text{-}BINOLate)]_2$	Ga_2O_2 ring	1.834(6)[a] 2.072(4)[b]	89.1(2) 89.6(2)	105.8(2)	[93]
151	$[Ga(hbo)_2(O,O'\text{-}CH_3CO_2)]$	O_4GaN_2 core, octahedral	1.873(2)	109.7(1)		[95]
152	$[EtGa(OCH_2CH_2NMe_2)_2]$	$RGaO_2N_2$ core, trigonal bipyramidal	1.8522(13) 1.8534(13)	114.94(6)		[4]
154	$[ClGa(OC(CF_3)_2CH_2NMe_2)_2]$	$ClGaO_2N_2$ core, trigonal bipyramidal	1.8605(16) 1.8625(16)	130.40(7)		[54]
155	$[ClGa(OC(CF_3)_2CH_2C(CH_3){=}NMe)_2]$	$ClGaO_2N_2$ core, trigonal bipyramidal	1.8364(19) 1.8432(18)	114.46(9)		[54]
	Indium bis(alkoxides)/(aryloxides)					
157	$[MeIn(O^tBu)_2]_2$	In_2O_2 ring, planar	2.006(4) 2.128(8)	76.4(2)	103.6(2)	[82]
159	$Li[(Ar^nO)_2InCl_2]$	InO_2Li ring, planar	2.136(4)	77.4(3)		[53]
Gallium Tris(alkoxides)/(aryloxides)						
161	$Ga[(\mu\text{-}O^iPr)_2Ga(O^iPr)_2]_3$	GaO_6 core, octahedral	1.814 (av.) 1.890 (av.) 1.997 (av.)[d]	75.3(2) 76.0(1)	101.3(1)–102.0(1)	[6]
168	$[Ga(\mu\text{-}OCMe_2Et)(OCMe_2Et)_2]_2$	Ga_2O_2 ring	1.768(2)–1.778(2)[a] 1.912(1)–1.917(1)	80.3(1)	104.3	[6]
169	$[Ga(O^tBu)_3(HNMe_2)]$	O_3GaN core, tetrahedral	1.799(2)–1.822(2)	114.2(3)–125.1(3)		[6]
178	$[Ga(OCH(CF_3)_2)_3(4\text{-}Me_2Npy)]$	O_3GaN core, tetrahedral	1.801(5) 1.804(5) 1.811(5)	110.5(2) 112.0(2) 115.0(2)		[5]
179	$[Ga(OCMe_2(CF_3))_3(4\text{-}Me_2Npy)]$	O_3GaN core, distorted tetrahedral	1.778(9) 1.80(1) 1.802(8)	110.3(4) 114.2(5) 117.0(4)		[5]
186	$[Ga(oz)_3]$	GaO_3N_3 core, octahedral	1.929(2)–1.981	91.91(9) 174.28(9)		[111]
189	$[Ga(aloz)_3]$	GaO_3N_3 core, octahedral	1.920(3)–1.938(2)	94.4(1)		[111]

Indium tris(alkoxides)/(aryloxides)						
196	$[In(\mu\text{-}O^tBu)(O^tBu)_2]_2$	In_2O_2 ring	1.969(4) 1.985(4) 2.107(3) 2.115(3)	77.05(13)[c] 106.97(15) 109.45(15) 117.25(16) 119.41(18) 119.84(17)	102.95(13)	[118]
201	$[In(OCMe_2(CF_3))_3]_2$	In_2O_2 ring, slightly folded	2.129(4) 2.134(5)	75.8(2)	103.5(5)	[118]
202	$In[(\mu\text{-}OCHEt_2)_2(OCHEt_2)_2]_3$	In_2O_2 ring	2.166(4)–2.182(4)	73.62(14)–74.16(15)[c]	104.02(16)–104.72(15)	[118]
204	$[In(ODipp)_3(H_2N^tBu)_2]$	O_3InN_2 core, tbp	2.0569(14) 2.0627(15) 2.0751(14)	116.74(6) 118.17(6) 125.00(6)		[118]
206	$[In(O^tBu)_3(Me_2Npy)_2]$	O_3InN_2 core, tbp	2.027(2) 2.037(2) 2.058(2)	99.42(11) 121.95(10) 138.59(10)		[118]
207	$[In(OCMeEt_2)_3(Me_2Npy)]$	O_3InN core, tbp with distortion towards tetrahedral	2.0139(16) 2.0153(15) 2.0282(15)	115.51(6) 116.27(7) 119.04(6)		[118]
208	$[In(OCH(CF_3)_2)_3(Htmp)]$	O_3InN core, tbp	2.0043(16) 2.0108(17) 2.0470(15)	104.94(7) 115.90(8) 110.67(8)		[7]
209	$[In(OCMe(CF_3)_2)_3(py)_3]$	O_3InN_3 core, distorted octahedral	2.0891(18) 2.1237(18) 2.1097(17)	98.85(8) 98.25(8) 162.79(7)		[7]
211	$[In(OCH_2CH_2NMe_2)_3]_2$	In_2O_2 ring	2.056(4)–2.189(4)	71.1(2) 71.4(2)	106.2(2) 108.3(2)	[119]
215	$[In(oz)_3]$	InO_3N_3 core, octahedral	2.103(2)–2.149(3)	96.77(7)		[111]

[a] Terminal M—O bond.

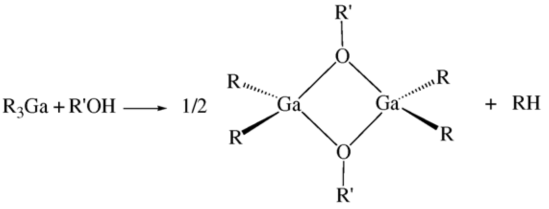
[b] Bridging M—O bond.

[c] Angles associated with the central M_2O_2 ring.

[d] $M—O_{terminal}$, $M^4—O_{bridge}$ and $M^6—O_{bridge}$.

CD_3, C_2H_5) were subsequently reported and the vibrational data (IR and Raman) indicated that the methyl derivatives are trimeric with puckered six-membered M_3O_3 ring systems [14]. The compounds $[Me(Cl)GaOMe]_n$, $[Cl_2Ga(OMe)]_n$ and $[Et_2Ga(OMe)]_n$ were also described. Similarly, the reaction of R_3Ga with 1 equiv. of ${}^tBuOH$ afforded the complexes $[R_2Ga(O^tBu)]_2$ (R = CH_3 (**2**), ${}^tBu$ (**3**)) [15,16]. Treatment of R_3Ga with excess ${}^tBuOH$ only resulted in the formation of **2** and **3**, as shown in Eq. (4). The lack of further reaction is probably due to electronic rather steric effects, since the strongly electron donating alkoxides in organogroup 13 metal complexes generally reduces the reactivity of the M–R bond towards protonolysis [17].

A series of related complexes were also prepared via the reaction of Me_3Ga with ROH to yield $[Me_2Ga(OR)]_n$ (R = ${}^tBu$, ${}^nBu$, Me, $PhCH_2$) and Et_3Ga with EtOH to give $[Et_2Ga(OEt)]_n$ [18–20]. Some of these compounds had been previously reported [15,16]. More recently, reaction of Me_3Ga with CyOH was shown to yield the dimeric complex $[Me_2Ga(OCy)]_2$ (**4**), via evolution of methane [21]. An X-ray structure determination showed that compound **4** is dimeric with a planar Ga_2O_2 ring (Ga–O 1.953(4) and 1.954(4) Å). In contrast to the formation of **4**, reaction of Me_3Ga with excess $PhCH_2OH$ resulted in the isolation of the sesquialkoxide $[Ga\{MeGa(OCH_2Ph)_3\}_3]$ [21].



2, R = Me, R' = ${}^tBu$; **3**, R = R' = ${}^tBu$, **4**, R = Me, R' = Cy;
11, R = ${}^tBu$, R' = Me; **12**, R = ${}^tBu$, R' = Et; **13**, R = ${}^tBu$, R' = ${}^nPr$;
14, R = ${}^tBu$, R' = ${}^iPr$; **15**, R = ${}^tBu$, R' = ${}^nBu$; **16**, R = ${}^tBu$, R' = ${}^iBu$;
17, R = ${}^tBu$, R' = ${}^sBu$; **18**, R = ${}^tBu$, R' = ${}^nC_5H_{11}$;
19, R = ${}^tBu$, R' = $CH_2CH_2{}^iPr$; **20**, R = ${}^tBu$, R' = $CHEt_2$;
21, R = ${}^tBu$, R' = $CH_2{}^tBu$; **22**, R = ${}^tBu$, R' = ${}^nC_6H_{13}$;
23, R = ${}^tBu$, R' = Cy; **24**, R = ${}^tBu$, R' = Ph; **25**, R = ${}^tBu$, R' = CH_2Ph;
26, R = ${}^tBu$, R' = $CH(CF_3)_2$

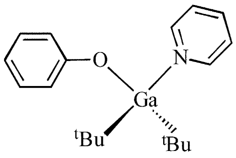
(4)

Oxidation of ${}^tBu_3Ga$ with oxygen resulted in the formation of the gallium peroxide $[{}^tBu_2Ga(OO^tBu)]_2$ [16]. Compound **3** was then isolated from the thermolysis of $[{}^tBu_2Ga(OO^tBu)]_2$, as shown in Scheme 2. Reaction of $[{}^tBu_2Ga(OO^tBu)]_2$ with 2 equiv. of PPh_3 resulted in the oxidation of PPh_3 and the formation of compound **3**, after hydrolysis. However, reaction of $[{}^tBu_2Ga(OO^tBu)]_2$ with 2 equiv. of PR_3 or $AsPh_3$, under anaerobic conditions, leads to the isolation of Lewis acid–base complexes $[{}^tBu_2Ga(O^tBu)(O{=}PR_3)]$ (**5**, R = Ph; **6**, R_3 = Ph_2Me; **7**, R = Et; **8**, R = ${}^nBu$; **9**, R = ${}^iPr$) and $[{}^tBu_2Ga(O^tBu)(O{=}AsPh_3)]$ (**10**). Compound **5** could also be prepared via the reaction of $[{}^tBu_2Ga(O^tBu)]_2$ with $O{=}PPh_3$.

Compounds of the type $[{}^tBu_2Ga(OR')]_2$ (R′ = Me (**11**), Et (**12**), ${}^nPr$ (**13**), ${}^iPr$ (**14**), ${}^nBu$ (**15**), ${}^iBu$ (**16**), ${}^sBu$ (**17**), ${}^nC_5H_{11}$ (**18**), $CH_2CH_2{}^iPr$ (**19**), $CHEt_2$ (**20**), $CH_2{}^tBu$ (**21**), ${}^nC_6H_{13}$ (**22**), Cy (**23**), Ph (**24**), CH_2Ph (**25**), $CH(CF_3)_2$ (**26**)) have been synthesised via the reaction of ${}^tBu_3Ga$ with R′OH, according to Eq. (4) [22,23]. The structures of **11**, **13**, **18**, **20**–**22**, **24** and **26** have been determined by X-ray crystallography, which showed that the complexes are dimeric. The geometry of the Ga_2O_2 core was found to be independent of the substituent at oxygen. The Ga–O and Ga–C bond distances for all the compounds are within the range expected (Ga–O 1.91–2.10 Å; Ga–C 1.96–2.16 Å). Steric interactions with the gallium *tert*-butyl groups were found to modify the conformation adopted by the alkoxide group. The crystal packing of $[{}^tBu_2Ga(OR')]_2$, where R′ = carbon chains of five or lower, is dependent on the packing of the organometallic $[{}^tBu_2Ga(\mu\text{-}O)_2Ga{}^tBu_2]$ core, whereas amphiphilic intermolecular interactions dominate the packing for longer carbon chain alkyl groups.

Two monomeric bis(*tert*-butyl)gallium alkoxides have been prepared and structurally characterised, as shown in Scheme 2 [24,25]. Reaction of ${}^tBu_3Ga$ with $HOCPh_3$ in refluxing hexane yielded $[{}^tBu_2Ga(OCPh_3)]$ (**27**) with evolution of butane. The aryloxide $[{}^tBu_2Ga(OC_6H_2\text{-}2,6\text{-}{}^tBu_2\text{-}4\text{-}Me)]$ (**28**) was isolated from the reaction of ${}^tBu_2GaCl$ and $LiOC_6H_2\text{-}2,4\text{-}{}^tBu_2\text{-}4\text{-}Me$. The structures of **27** and **28** consist of monomeric units with the gallium centre adopting distorted trigonal planar coordination geometries (**27**; Ga–O 1.831(4) Å, O–Ga–C 115.0(2)° and 118.2(2)°; **28**, Ga–O 1.821(3) Å, O–Ga–C 106.7(2)° and 123.2(1)°). In the structure of **27**, the orientation of the CPh_3 fragment is such as to preclude a π-type interaction between the vacant pz-orbital on gallium and the oxygen lone pair. However, there is a short intramolecular contact with the carbon atoms of one of the phenyl groups (Ga···C 2.894(6) Å).

Lewis acid–base adducts similar to compounds **5**–**10** have also been reported [26,27]. Reaction of $[{}^tBu_2Ga(OPh)]_2$ (**24**) with pyridine resulted in cleavage of the Ga_2O_2 core and formation of $[{}^tBu_2Ga(OPh)(py)]$ (**29**). Similarly, reaction of compound **24** with wet pyrazine (pyz, $N_2C_4H_4$) resulted in the isolation of $[{}^tBu_2Ga(OPh)(pyz)]\cdot PhOH$ (**30**). The geometry of the phenoxide oxygen in the structure of **29** is significantly different from **30** due to the O···H–O hydrogen bond to phenol in **30**, as shown by the N–Ga–O–C torsion angle of 131.2° in **29** and 180° in **30**.



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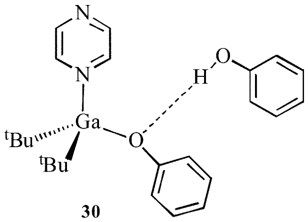
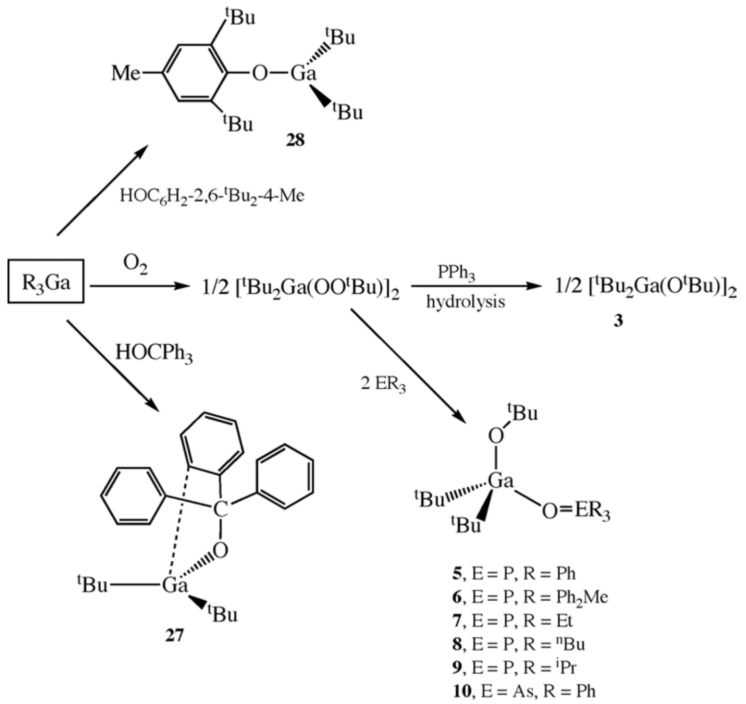


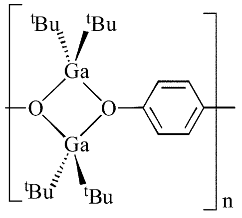
30

The gallium aryloxide polymer, $[\{{}^tBu_2Ga\}_2(\mu\text{-}OC_6H_4O)]_n$ (**31**) was synthesised by the reaction of hydroquinone with ${}^tBu_3Ga$ [27]. Reacting compound **31** with pyridine resulted in the cleavage of the Ga_2O_2 dimeric core to afford the monomeric compounds $[\{{}^tBu_2Ga(L)\}_2(\mu\text{-}$



Scheme 2.

$OC_6H_4O)]$ (**32**, L = py; **33**, L = 4-Mepy; **34**, L = 3,5-Me_2py). Related reactions of $^tBu_3Ga$ with diols have also been reported [28].



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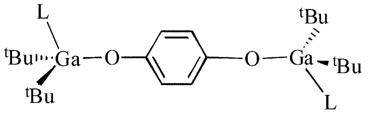
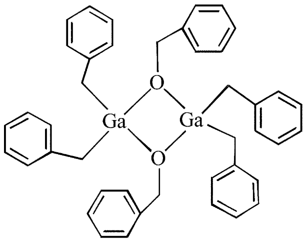


32, L = py
33, L = 4-Mepy
34, L = 3,5-Me_2py

Reaction of $(PhCH_2)_3Ga$ with dry oxygen in toluene resulted in the isolation of $[(PhCH_2)_2Ga(OCH_2Ph)]_2$ (**35**) [29]. Compound **35** was also prepared by treatment of $(PhCH_2)_3Ga$ with $PhCH_2OH$. The dimeric nature of **35** was confirmed by X-ray diffraction, which showed that the benzyl substituents create a propellor-shaped molecule. The Ga–O bond distances of 1.951(2) and 1.950(2) Å are similar to the dimeric complexes **11**, **13**, **18**, **20**–**22**, **24** and **26**. The related dimer $[[(PhCH_2)_2Ga(O^tBu)]_2$ (Ga–O 1.931(3) and 1.950(3) Å; O–Ga–O 78.8(1)°; Ga–O–Ga 101.2(1)°) was isolated from the reaction of $[(PhCH_2)_2GaCl]$ and ^tBuOLi [30].

The dimeric compound $[(\eta^1\text{-Cp})_2Ga(OEt)]_2$ (**36**) was obtained by treatment of LiCp with $GaCl_3$ in diethylether (Et_2O) at ambient temperature [31]. At low temperature the same reaction results in the formation of Cp_3Ga and it was presumed that the higher reaction temperature allowed a $GaCl_3$-promoted cleavage of Et_2O. Compound **36** was the first structurally characterised simple gallium alkoxy compound. The structure of **36** consists of dimeric molecules with a Ga_2O_2 four-membered ring (Ga–O 1.940(3) and 1.906(3) Å). The cyclopentadienyl groups are bonded to gallium in the η^1 manner.



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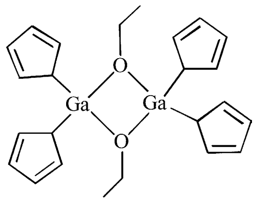
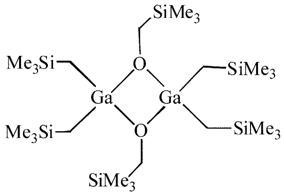


36

A similar dimeric structure was observed for $[\{(Me_3Si)CH_2\}_2Ga(OCH_2(SiMe_3))]$ (**37**) [32]. The endocyclic angles in **37** are O–Ga–O 81.6(1)° and Ga–O–Ga 98.4(1)°. The exocyclic angles are increased due to steric demands of the bulky $CH_2(SiMe_3)$ groups (C–Ga–C 126.8(2)°). The Ga–O bond lengths (1.967(4) Å) agree well with related complexes, such as **35** [28].



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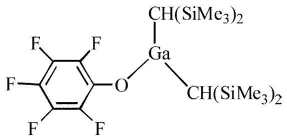
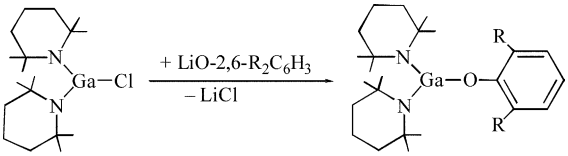


38

A novel approach for the generation of a dialkylgallium alkoxide involved the reaction of the digallane, $R_2Ga–GaR_2$

($R = CH(SiMe_3)_2$) with C_6F_5OH [33]. The mononuclear gallium pentafluorophenolate $[\{(Me_3Si)_2CH\}_2Ga(OC_6F_5)]$ (**38**) was isolated via cleavage of the Ga–Ga bond. The crystal structure of **38** revealed that the gallium atom is planar with a Ga–O bond distance of 1.843 Å. The Ga–O–C angle to the pentafluorophenolate group is enlarged to 131.6°.

Salt elimination routes were used to prepare $[(tmp)_2Ga(O\text{-}2,6\text{-}R_2C_6H_3)]$ (R = H (**39**), Me (**40**)) via the reaction of $[(tmp)_2GaCl]$ with $LiO\text{-}2,6\text{-}R_2C_6H_3$, as shown in Eq. (5) [34]. The X-ray crystal structure of **39** revealed that the gallium centre adopts a trigonal planar geometry with an N–Ga–N angle of 133.9(1)°. Thus, compound **39** is monomeric and the geometry around one nitrogen atom is planar, the other nitrogen atom shows slightly pyramidal coordination geometry. The result of this is that the two Ga–N bond distances in **39** are quite different (Ga–N 1.849(1) and 1.818(1) Å). A related (alkoxy)gallium amide, $[(tmp)Ga(\mu\text{-}OEt)Cl]_2$ (**41**) has also been reported [35]. The solid-state structure of **41** comprises dimeric molecules in which the OEt groups act as bridging ligands.

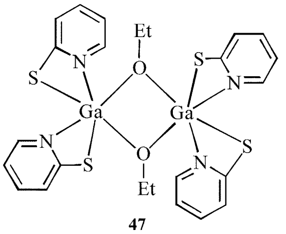


39, R = H
40, R = Me

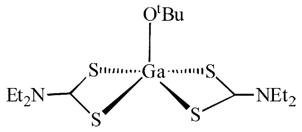
(5)

The synthesis and structure of two (alkoxy)gallanes, $[H_2Ga(O^tBu)]_2$ (**42**) and $[H_2Ga(OCH^tBu_2)]_2$ (**43**) have been reported, as shown in Scheme 3 [36,37]. Compound **42** was synthesised by the 1:1 reaction of $[GaH_3(OEt_2)]$ and ^tBuOH in diethyl ether at 0 °C, followed by sublimation. The correct stoichiometry of the reaction is important for obtaining the desired product. The solid-state structure of **42** comprises dimeric molecules with a planar Ga_2O_2 core (O–Ga–O 78.6(5)°; Ga–O–Ga 101.4(5)°). The gallium centres in **42** adopt distorted tetrahedral coordination geometry. The coordination at oxygen is planar and the Ga–O bond lengths (1.908(9) and 1.902(9) Å) fall within the predicted single bond ranges. The structure of **42** is similar to compound **43** in that they form comparable dimers by oxygen bridging. However, the mean Ga–O–Ga bond angle in **43** is 99.3(3)°, which is 2.1° less than in compound **42**. In addition the Ga–O bond distances in **43** (1.93(1) Å) are longer than those observed in **42**. These differences can be attributed to the presence of the bulkier CH^tBu_2 group in **43** in contrast to *tert*-butyl group in **42**. Interestingly, *tert*-butoxygallane (**42**) reacted with tetraphenyl-1,3-disiloxanediol, $HO(Ph_2)Si–O–Si(Ph_2)OH$ to yield the bicyclic compound $[(OSiPh_2OSiPh_2O)[Ga(H)]_2(O^tBu)_2]$ (**44**) [38]. In contrast, a change in the molar ratio of **42** to $HO(Ph_2)Si–O–Si(Ph_2)OH$ to 1:2 afforded two new products, $[(OSiPh_2OSiPh_2OSiPh_2O)GaH]_2$ (**45**) and $[(OSiPh_2OSiPh_2OSiPh_2O)GaO^tBu]_2$ (**46**).

The alkoxy-thiolate and dithiocarbamate compounds $[Ga(OEt)(SC_5H_4N)_2]_2$ (**47**) and $[Ga(O^iPr)(S_2CNEt_2)_2]$ (**48**) have been prepared [39,40]. Compound **47** was synthesised from $GaCl_3$, HSC_5H_4N and NEt_3 in ethanol solution. The structure of **47** is dimeric via alkoxide bridges with the gallium centres in distorted octahedral geometries. The Ga–O bond distances are 1.955(3) and 1.944(3) Å. Compound **48** was synthesised from the in situ reaction of $[^tBuGa(S_2CNEt_2)_2]$ with acetone in hexane solution. Thus, the compound $[^tBuGa(S_2CNEt_2)_2]$ has reduced the ketone to form the alkoxide **48**. The crystal structure of **48** revealed that it is monomeric with square-based pyramidal coordination geometry. The Ga–O bond distance is 1.93(1) Å and the O–Ga–S angles vary from 97.2(4)° to 123.1(4)°.

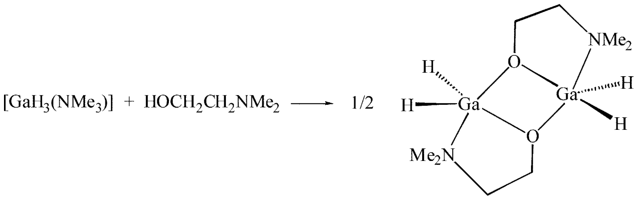


47



48

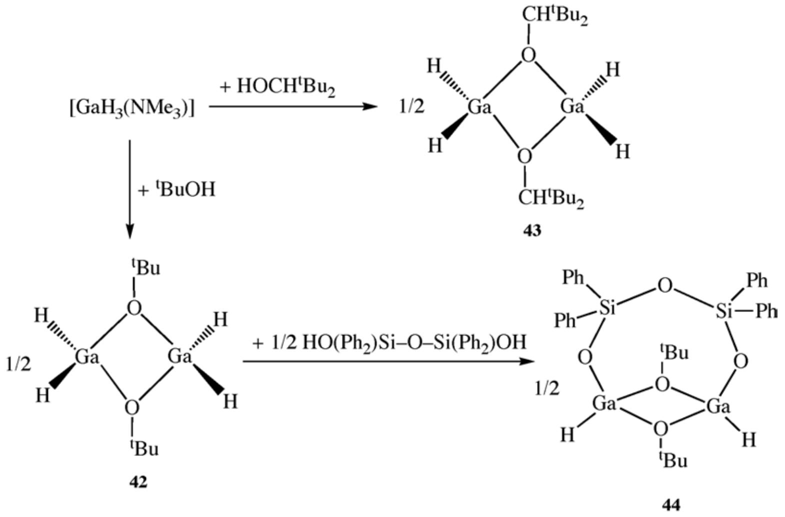
A range of gallium monoalkoxides incorporating donor functionalised alkoxides have been described, the first of which was reported in 1953 [13]. The first complex of this kind to be crystallographically characterised was reported almost 20 years later by Rettig et al. [41]. Reaction of Me_3Ga with *N*,*N*-dimethylethanolamine ($HOCH_2CH_2NMe_2$) in a 1:1 ratio afforded colourless crystals of $[Me_2Ga(OCH_2CH_2NMe_2)]_2$ (**49**), as shown in Scheme 4. Similarly, treatment of $[GaH_3(NMe_3)]$ with $HOCH_2CH_2NMe_2$ yielded $[H_2Ga(OCH_2CH_2NMe_2)]_2$ (**50**), according to Eq. (6).



50

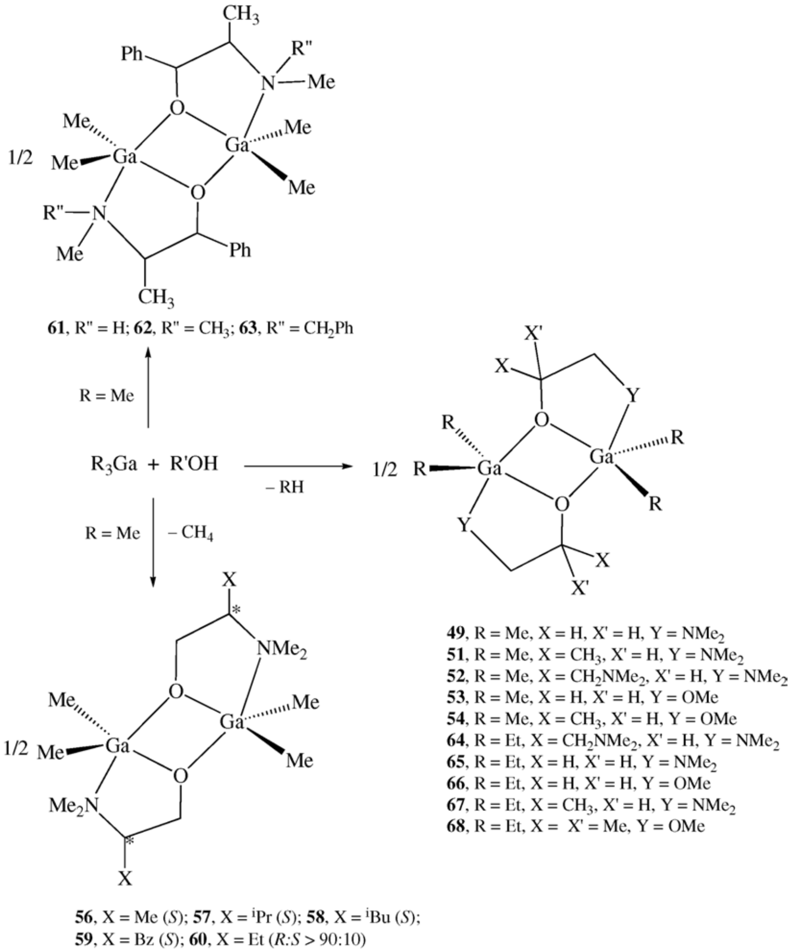
(6)

The crystal structures of **49** and **50** were investigated by X-ray diffraction and showed dimers with the formation of four-membered Ga_2O_2 rings resulting in centrosymmetric molecules with three fused rings. The gallium centres in **49** and **50** adopt distorted trigonal bipyramidal coordination geometries with the nitrogen atoms occupying axial positions and the oxygen atoms occupying an equatorial site on one gallium and an axial position on the second gallium atom. The two remaining equatorial positions are occupied by methyl groups in **49** and hydrogen atoms in **50**. The Ga_2O_2 rings in **49** and **50** are planar with Ga–O (equatorial and axial) bond distances of 1.913(3) and 2.078(3) Å in **49** and 1.911(3) and 2.053(3) Å in **50**. The equatorial Ga–O bond



Scheme 3.

distances are shorter than the axial Ga–O bond distances, indicative of two active bonding Ga–O bond types (Fig. 1). The angles at Ga and O are 74.6(1)° and 105.4(1)° in **49** and 74.7(1)° and 105.3(1)° in **50**. The Ga–N bond distances in the dimethylgallium derivative **49** (2.471(4) Å) are longer than the corresponding gallane compound **50** (2.279(3) Å) due to steric interactions. Interestingly, a weak Ga–N bond in **49** can be used to explain the original prediction of a four-



61, R" = H; **62**, R" = CH$_3$; **63**, R" = CH$_2$Ph

49, R = Me, X = H, X' = H, Y = NMe$_2$
51, R = Me, X = CH$_3$, X' = H, Y = NMe$_2$
52, R = Me, X = CH$_2$NMe$_2$, X' = H, Y = NMe$_2$
53, R = Me, X = H, X' = H, Y = OMe
54, R = Me, X = CH$_3$, X' = H, Y = OMe
64, R = Et, X = CH$_2$NMe$_2$, X' = H, Y = NMe$_2$
65, R = Et, X = H, X' = H, Y = NMe$_2$
66, R = Et, X = H, X' = H, Y = OMe
67, R = Et, X = CH$_3$, X' = H, Y = NMe$_2$
68, R = Et, X = X' = Me, Y = OMe

56, X = Me (*S*); **57**, X = ^{i}Pr (*S*); **58**, X = ^{i}Bu (*S*);
59, X = Bz (*S*); **60**, X = Et (*R*:*S* > 90:10)

Scheme 4.

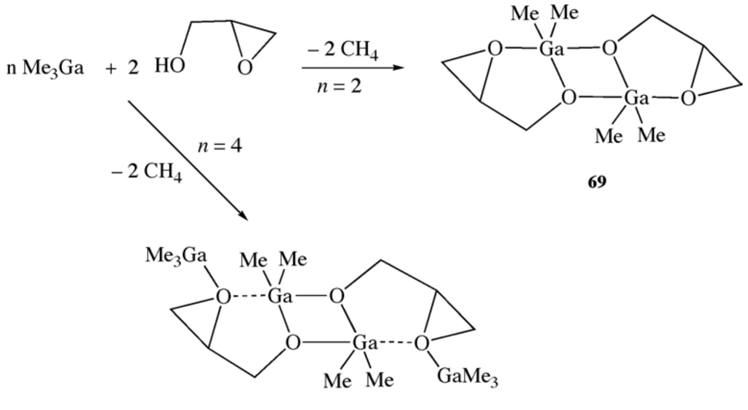
coordinate gallium structure for the dimer, which involved a Ga_2O_2 ring but without coordination of nitrogen atoms to the gallium centres [13].

More recently, there has been significant interest in the development of intramolecularly stabilised gallium monoalkoxides due to their application in organic synthesis and CVD (Section 5) [1,2,4]. Thus, reaction of Me_3Ga with R′OH resulted in the isolation of the dimeric complexes $[Me_2Ga(OR')]_2$ (R′ = $CH(CH_3)CH_2NMe_2$ (**51**) [42], $CH(CH_2NMe_2)_2$ (**52**) [43], CH_2CH_2OMe (**53**), $CH(CH_3)CH_2OMe$ (**54**) and $CH_2CH_2C(CH_3)_2OMe$ (**55**) [44]), which are similar to compound **49** (Scheme 4) [41]. Related reactions between Me_3Ga and optically active alcohols yielded $[Me_2Ga(OCH_2CHXNMe_2)]_2$ (X = Me (*S*) (**56**), ^{i}Pr (*S*) (**57**), ^{i}Bu (*S*) (**58**), Bz (*S*) (**59**) and Et (*R*:*S* > 90:10 (**60**)) [45]. In addition, treatment of Me_3Ga with (1*R*, 2*S*)-PhCH(OH)CH(CH_3)NR″CH_3 afforded the chiral dimethylgallium complexes [(1*R*, 2*S*)-($Me_2Ga(OCH(Ph)CH(CH_3)NR''CH_3)]_2$ (R = H (**61**), CH_3 (**62**) and Bz (**63**)) [46]. The enantioselective isocyanosilylation of *meso* cyclohexene oxide with trimethylsilyl cyanide (TMSCN) has been examined using these chiral organogallium complexes (Section 5). The structures of **51–54**, **57**, **59–61** have been determined and revealed that all the complexes are oxygen-bridged dimers with planar or nearly planar Ga_2O_2 rings. The gallium centres are coordinated in a distorted trigonal bipyramidal geometry and therefore the structures are similar to compound **49** with comparable bond lengths and angles (Table 1) [41].

The related diethylgallium alkoxides incorporating donor functionalised ligands have also been reported [4,47]. Thus, the 1:1 reaction of Et_3Ga with R′OH afforded the dimeric complexes $[Et_2Ga(OR')]_2$ (R′ = $CH(CH_2NMe_2)_2$ (**64**), $CH_2CH_2NMe_2$ (**65**), CH_2CH_2OMe (**66**), $CH(CH_3)CH_2NMe_2$ (**67**) and $C(CH_3)_2CH_2OMe$ (**68**)), as shown in Scheme 4. Unfortunately, no structural data are available for compounds **64–68**. However, the dimeric nature of **64–68** was confirmed by mass spectroscopy and the Ga_2O_2 moiety of the dimers display strong absorptions in the FT-IR (503 and 435 cm^{-1}). Compounds **49**, **53–60** and have been used to cross-alkylate aryl iodides, bromides and triflates in the presence of a transition metal catalyst, whereas compounds **64** and **68** have been shown to deposit Ga_2O_3 films via CVD (Section 5).

The structures of the dialkylgallium alkoxide complexes containing donor functionalised (O,N′ and O,O′) ligands gives some information regarding the relationship between ligand design and strength of the axial Ga–N and axial Ga–O bonding. In general, the O,O′ (e.g. OCH_2CH_2OMe) donor functionalised ligands exhibit stronger stabilising dative bonding interactions with gallium than the O,N′ ligands (e.g. $OCH_2CH_2NMe_2$). This is due to unfavourable steric interactions, which arise between the alkyl groups of the amine ligand and the alkyl groups bonded to the gallium centre. Furthermore, bulkier and more rigid chelating ligands show weaker or stronger dative bonding due to the associated steric and conformational constraints. A dative ligand–metal interaction in compounds with no structural data are confirmed by a comparison of proton resonances of the alkoxide ligand in the product to the free ligand. For example, in the ^1H NMR of **64–68** a downfield shift in the resonance of protons positioned α to the donor heteroatom is observed [4].

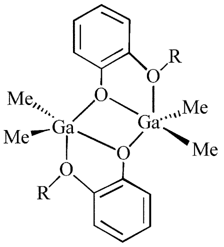
The 1:1 reaction of Me_3Ga and 2,3-epoxy-1-propanol resulted in the formation of the dimeric species $[Me_2Ga(OCH_2\overline{CHCH_2O})]_2$ (**69**), as shown in Scheme 5 [48]. The ^1H NMR indicated that the structure of **69** is similar to the aforementioned dialkyl gallium alkoxides derived from donor functionalised alcohols, for example, **49**, **51–54** [41–44]. The ^1H NMR of **69** shows the presence of *R*, *S* and *R**, *R** diastereoisomers. Unfortunately, no structural data are available for compound **69**. However, reacting 2 equiv. of Me_3Ga with 2,3-epoxy-1-propanol afforded the tetranuclear adduct $[Me_2Ga(OCH_2\overline{CHCH_2O})GaMe_3]_2$ (**70**), according to Scheme 5.



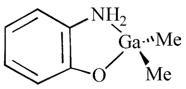
Scheme 5.

The X-ray structure of **70** revealed that the epoxide oxygen atoms double coordinate to different Lewis acid centres. Thus, compound **70** can be viewed as the Lewis acid–base adduct of Me_3Ga with the dimeric compound **69**, such that two Me_3Ga moieties are coordinated to the epoxide oxygen atoms. The central Ga_2O_2 ring in **70** is planar with the epoxide oxygen atoms being in the same plane. The central gallium atoms adopt a distorted trigonal bipyramidal geometry with Ga–O bridging bond distances of 1.951(3) and 1.991(3) Å. The central Ga–O(epoxide) bond distance is long (2.886(3) Å) but significantly shorter than the sum of the van der Waals radii of oxygen and gallium (3.39 Å). The significance of compound **70** is that the epoxide has been shown to be activated by two independent Lewis acid centres.

The reaction of trialkylgallium with a range of phenols and benzylalcohols incorporating intramolecularly coordinating ligands has also been reported. Treatment of Me_3Ga with HOC_6H_4-2-OR resulted in the isolation of $[Me_2Ga(OC_6H_4\text{-}2\text{-}OR)]_2$ (**71**, R = Me; **72**, R = Et) [42,44,49]. The structure of **71** comprises dimeric molecules with a planar four-membered Ga_2O_2 ring [49]. The aromatic rings in **71** lie in the same plane as the Ga_2O_2 ring with the 2-methoxy groups orientated “anti” to each other. The 2-methoxy groups interact with the gallium atoms resulting in a trigonal bipyramidal Ga centre similar to the dimeric complexes **51–54** [41–43]. The bridging Ga–O distances differ in length (1.957(4) and 2.046(4) Å) and are shorter than the Ga–OMe bond distance (2.521(5) Å). In contrast to the formation of dimeric **71** and **72**, reaction of Me_3Ga with HOC_6H_4-2-NH_2 afforded the monomeric complex $[Me_2Ga(OC_6H_4\text{-}2\text{-}NH_2)]$ (**73**) [50]. The structure of **73** consists of individual monomer units linked to neighbouring units by a network of N–H···O hydrogen bonds. Unfortunately, disordering of the *o*-aminophenolato ligand resulted in averages of the actual Ga–N and Ga–O distances being obtained.

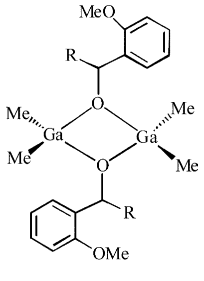


71, R = Me; **72**, R = Et



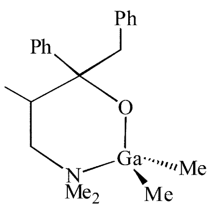
73

Treatment of Me_3Ga with the related alcohols, 2-methoxybenzyl alcohol and *o*-methyoxyphenyl-1-ethanol afforded the dimeric complexes $[Me_2Ga(OCHRC_6H_4\text{-}2\text{-}OMe)]_2$ (**74**, R = H; **75**, R = Me) [44,51]. The dimeric nature of compound **75** was confirmed by X-ray diffraction and revealed a planar Ga_2O_2 core. The Ga–O distances 1.951(2) and 1.957(2) Å are similar to those observed in other dimeric complexes, for example compound **70** [47]. Interestingly, the gallium atoms adopt a tetrahedral coordination geometry. Therefore, the oxygen atoms of the methoxy substituents do not coordinate to the gallium centre. This is in contrast to the aluminium analogue of compound **74** (R = H), where the MeO group coordinates to the Al centre (Al–O 2.572(2) Å), however, no structural data are available for **74** [44]. It is possible that in compound **74** the oxygen atom of the methoxy group does coordinate to the gallium centre but in compound **75**, the presence of the methyl substituent, prevented coordination.

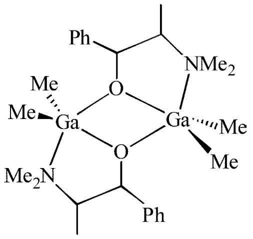


74, R = H
75, R = Me

The optically active aminoalcohols (−)-(1*R*,2*S*)-2-dimethylamino-1-phenylpropanol and (+)-(2*SR*,3*R*)-4-dimethylamino-3-methyl-1,2-diphenyl-2-butanol react with Me_3Ga to produce the dimethylgallium alkoxides $[Me_2Ga(OCPh(CH_2Ph)CH(CH_3)CH_2NMe_2)]$ (**76**) and $[Me_2Ga(OCH(Ph)CH(CH_3)NMe_2)]_2$ (**77**) [52]. The structures of **76** and **77** have been determined and as expected compound **77** is dimeric in the solid state. The gallium centre in compound **77** is penta-coordinate, as observed in other dimeric dialkylgallium alkoxides. In contrast, compound **76** is monomeric suggesting that dimerisation via formation of a four-membered Ga_2O_2 ring is prevented. The presence of a phenyl and a benzyl group close to the oxygen atom in **76** inhibits the formation of dimers via oxygen-bridging due to steric reasons. In addition, the formation of a six-membered ring in **76** provides stabilisation for the monomer. Therefore, the gallium centre in **76** is in a tetrahedral coordination environment. Interestingly, the Ga–N bond distance in **76** (2.11 Å) is shorter than in **77** (2.36 Å), which in solution dissociates, as shown by ^1H NMR studies. The Ga–O bond distances also vary between the two complexes, as expected for terminal versus bridging Ga–O bonds (**76**, Ga–O 1.846(2) Å; **77**, Ga–O 1.911(3) and 2.128(3) Å).

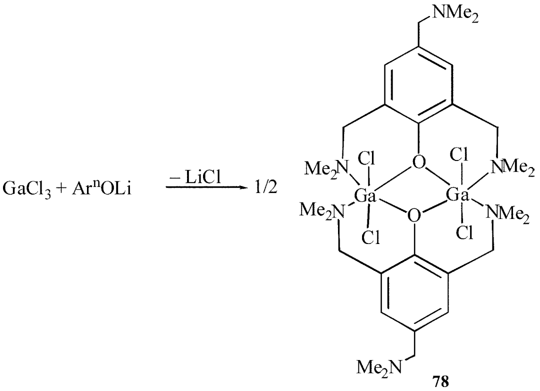


76



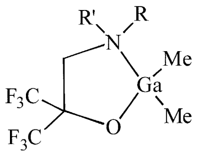
77

The dichloro(aryloxide)gallium complex $[Ar^nOGaCl_2]_2$ (**78**) (Ar^n = 2,4,6-tris(dimethylaminomethyl)phenyl) has been synthesised from the reaction of $GaCl_3$ with $LiOAr^n$ [53]. Unfortunately, no structural data are available for compound **78**. However, the dimeric nature of **78** was confirmed by mass spectral data. Compound **78** is thought to adopt the structure shown in Eq. (7) with bridging aryloxide ligands based on the related indium complex [Li(Ar^{n}O)$_2$InCl$_2$] (**159**) (Section 3.2).

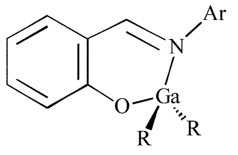


78 (7)

In contrast to the formation of the dimeric complexes **51–54**, the reaction of Me$_3$Ga with fluorinated aminoalcohols resulted in the isolation of the monomeric complexes [Me$_2$Ga(OC(CF$_3$)$_2$CH$_2$NRR′)] (**79**, R = H, R′ = Me; **80**, R = H, R′ = ^{t}Bu; **81**, R = R′ = Me) [54]. The structure of compound **81** was determined and revealed that the gallium centre is four-coordinate and adopts a distorted tetrahedral environment with bond angles in the range 107.6–125.0°. The Ga–N bond distance of 2.082(2) Å is significantly shorter than the Ga–N bond length observed in related dimeric gallium complexes incorporating non-fluorinated aminoalkoxide ligands, such as [Me$_2$Ga(OCH(CH$_3$)CH$_2$NMe$_2$)]$_2$ (Ga–N 2.525(2) Å) [42]. Thus, it appears that the coordinative unsaturation of the gallium atom in **81** is satisfied by the dative interaction with the nitrogen atom. In addition, the presence of electron-withdrawing CF$_3$ groups on the aminoalkoxide, as well as steric repulsion, reduces the bridging capability of the oxygen atom and prevents dimer formation. The Ga–O bond distance of 1.890(2) Å is comparable to that observed in the monomeric compound **76** [51].

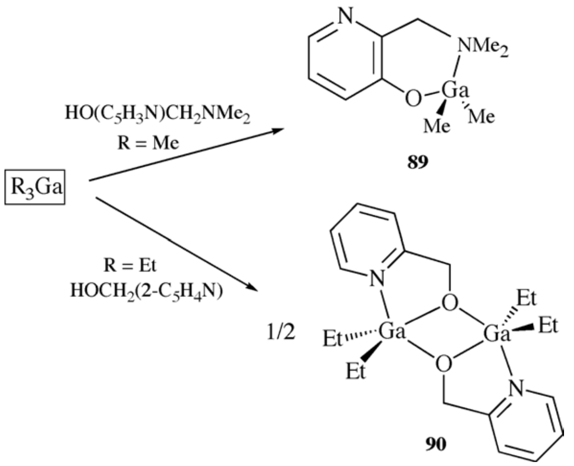


79, R = H, R' = Me
80, R = H, R' = ^{t}Bu
81, R = R' = Me

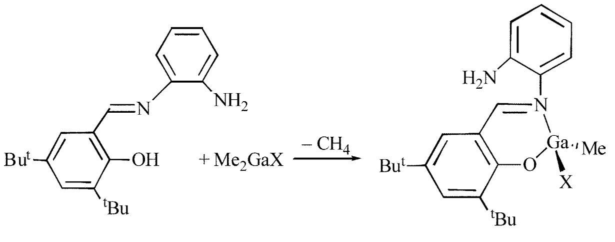


82, R = Me, Ar = Ph
83, R = Me. Ar = 2-py
84, R = Et, Ar = 2-py
85, R = Me, Ar = 2-MeOC$_6$H$_4$
86, R = Et, Ar = 2-MeOC$_6$H$_4$

Monomeric intramolecularly coordinated gallium complexes were also prepared from the reaction of R$_3$Ga with the Schiff-base ligands, *N*-phenylsaliclideneimine, *N*-salicylidene 2-aminopyridine or *N*-salicylidene 2-methoxyaniline to yield compounds **82–86** [55,56]. Some of these complexes were prepared as potential organic electroluminescent (OEL) substances. The molecular structures of compounds **82** and **83** were determined by X-ray crystallography, which revealed monomeric structures with the gallium atom in a distorted tetrahedron. Therefore, the N atom of the enamine group coordinates to the gallium atom (**82**, Ga–N 2.023(3) Å; **83**, Ga–N 2.059(2) Å) with a bond distance similar to that observed in monomeric **81** [54]. Interestingly, in the structure of **83**, the pyridyl group is close to the gallium atom (∼2.7 Å), suggesting that there is some interaction between the nitrogen of the pyridine ring and the gallium atom. This causes some distortion of bond angles around the gallium atom (e.g. O–Ga–N 90.76(7)°; C–Ga–C 131.2(1)°). The Ga–O bond length is 1.889(3) Å in **82** and 1.917(2) Å in **83** and comparable to complex **81** [53]. The related reaction between salicylidene(1-iminophenylene-2-amine) and Me$_3$Ga or Me$_2$GaCl afforded the monomeric complexes **87** and **88**, as shown in Eq. (8) [57]. The crystal structure of **87** reveals that the pendant amine arm is oriented away from the gallium atom, which is tetrahedral. The Ga–O (1.893(2) Å) and Ga–N (2.028(2) Å) bond distances are similar to compounds **82** and **83** [55,56]. The synthesis and spectroscopic characterisation of some related complexes [Me$_2$Ga(OC$_6$H$_4$-2-CH=NNHPh)] have also been reported via the reaction of the alcohol with Me$_3$Ga [58].



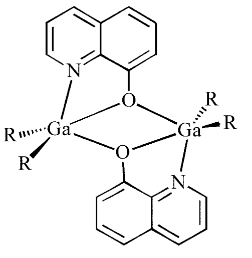
Scheme 6.



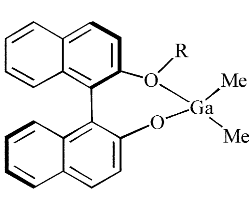
87, X = Me
88, X = Cl (8)

A series of dialkylgallium alkoxides incorporating pyridyl groups have been synthesised as shown in Scheme 6 [59,60]. X-ray crystallographic studies show that compound **89** is monomeric whereas compound **90** is dimeric [60,61]. The gallium centre in **89** is tetrahedrally coordinated with a Ga–N bond distance of 2.127(4) Å. The Ga–O bond distance is 1.892(3) Å, similar to related monomeric complexes, for example compound **82** [54]. The formation of a monomer is probably due to geometric constraints of having the O atom directly bonded to the pyridine ring. In contrast to **89**, the structure of **90** is dimeric and similar to other dimeric dialkylgallium donor functionalised alkoxides **51**–**54** [41–43]. All bond lengths and angles in **90** are typical for five-coordinate Ga (Ga–O 1.914(2) and 2.092(4) Å; Ga–N 2.269(3) and 2.302(3) Å).

Two dialkylgallium alkoxide complexes containing quinoline ligands have also been reported [61,62]. Thus, treatment of R_3Ga with 8-hydroxyquinoline afforded the dimeric complexes $[R_2Ga(Oquin)]_2$ (**91**, R = Me; **92**, R = cyclopentyl). The structures of **91** and **92** contain an oxygen-bridged coplanar Ga_2O_2 four-membered ring. The gallium atoms in **91** and **92** are five-coordinate with a distorted trigonal bipyramidal geometry. The Ga–O bond lengths (Ga–O: **91**, 1.937(3) and 2.297(3) Å; **92**, 1.941 and 2.342 Å) and Ga–N bond distances (Ga–N: **91**, 2.211(3) Å; **92**, 2.209 Å) in **91** and **92** are similar. The related compound $[Et_2Ga(Oquin)]$ was also reported and it was suggested that this compound was monomeric [63].



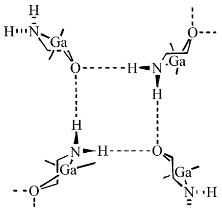
91, R = Me
92, R = Cyclopentyl



93, R = Me
94, R = Bz
95, R = ^{t}Bu

The related compounds $[Me_2Ga(BINOL\text{-}R)]$ (**93**, R = Me; **94**, R = CH_2Ph; **95**, R = ^{t}Bu) were synthesised from the treatment of binapthol monoethers (*R*)-BINOL-Me, (*R*)-BINOL-Bz and (*R*)-BINOL-^{t}Bu with 1 equiv. of Me_3Ga [64]. Unfortunately, no structural data are available for compounds **93**–**95**, however the compounds are thought to be monomeric based on mass spectral evidence. These compounds were investigated as catalysts for the enantioselective isocyanosilylation of *meso* epoxides with trimethylsilyl cyanide.

An interesting series of compounds are the dimethylgallium derivatives of amine alcohols, $[Me_2Ga(O\text{–}R\text{–}NH_2)]$ [65,66]. Compounds of this type demonstrate how hydrogen bonding can compete with metal–ligand coordination preferences and how conformational changes in a ligand and increased steric bulk can effect molecular aggregations. The compounds $[Me_2Ga(O\text{–}R\text{–}NH_2)]_n$ (**96**, $n = 1$, R = CH_2CH_2; **97**, $n = 1$, R = $CH_2CH_2CH_2$; **98**, $n = 2$, R = $CH_2CH(CH_3)$) were prepared from the reaction of Me_3Ga with the appropriate aminoalcohol. The structure of **96** consists of monomeric units with the gallium centre adopting a distorted tetrahedral geometry. Each monomer unit is linked to four others by an extensive network of N–H···O hydrogen bonds [65]. The crystal structure of **97** also comprises of monomeric molecules in which the gallium centre is tetrahedral (av. Ga–O 1.879 Å; av. Ga–N 2.073 Å) [66]. The six-membered GaOCCCN rings in **97** adopt a chair-like conformation. The monomeric molecules are linked by the alkoxide oxygen and amine nitrogen atoms acting as hydrogen donors and acceptors, resulting in a fully hydrogen-bonded network. Overall, the molecules of **97**, in the ribbon assemble with pairs of strongly hydrogen-bonded chains. The chains are cross-linked by weak N–H···O interactions.



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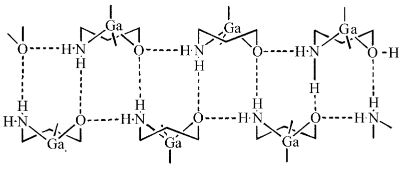
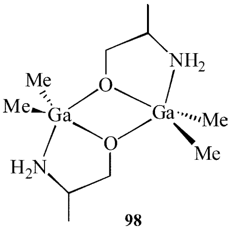


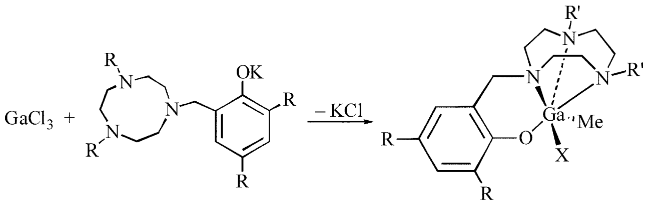
97

In contrast to the four-coordinate hydrogen-bonded polymeric structures of **96** and **97**, compound **98** is dimeric. There are no unusually short intermolecular contacts. The structure of **98** is similar to the dimeric dialkylgallium aminoalkoxides **51**–**54** (compound **98**; Ga–O 1.923 and 2.113 Å; Ga–N 2.348 Å) [41–43]. The formation of a dimer rather than a polymer in the structure of **98** is probably due to the substitution of a hydrogen by a methyl group in the carbon atom adjacent to the hydrogen donor, weakening the intermolecular hydrogen bond interactions and enforcing the structural changes.



98

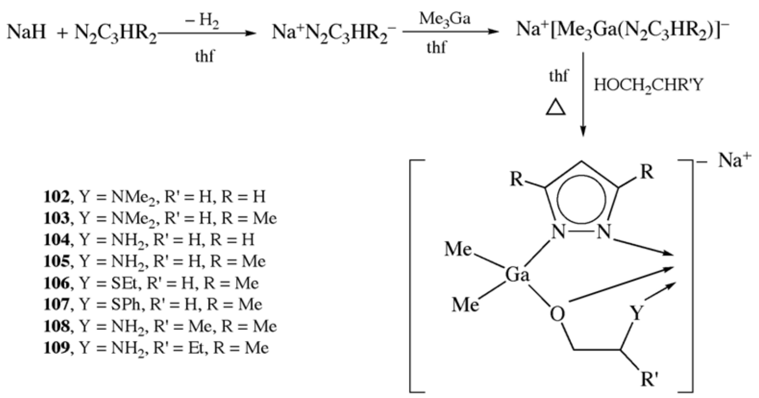
The mono-pendant arm triazacyclononane gallium complexes (**99**–**101**) have been reported recently, as shown in Eq. (9) [67]. The reaction of $KL^{a–c}$ with $GaCl_3$ gave the monomeric derivatives $[Ga(\kappa^4\text{-}L^{a–c})Cl_2]$ (**99**, L^a, R = ^{t}Bu, R′ = Me; **100**, L^b, R = ^{t}Bu, R′ = ^{i}Pr; **101**, L^c, R = Me, R′ = ^{i}Pr). Unfortunately, no structural data are available for **99**–**101**, however support for the proposed structures was obtained from the crystal structure of the indium analogue $[In(\kappa^4\text{-}L^b)Cl_2]$ (**140**) (Section 3.2). Further support for the κ^4-coordinated structures for **99**–**101** was obtained from NMR studies.



L^a: R = ^{t}Bu, R' = Me
L^b: R = ^{t}Bu, R' = ^{i}Pr
L^c: R = Me, R' = ^{i}Pr

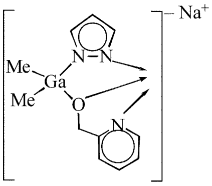
99, R = ^{t}Bu, R' = Me
100, R = ^{t}Bu, R' = ^{i}Pr
101, R = Me, R' = ^{i}Pr

(9)



Scheme 7.

A range of anionic dimethylgallium monoalkoxides incorporating pyrazolyl (pz) have been reported, as shown in Scheme 7. These salts were prepared by reacting $Na[Me_3Ga(L)]$ (L = pz or 3,5-Me_2pz) with the appropriate amino alcohol until cessation of methane evolution to afford compounds **102–105** (Scheme 7) [68,69]. This was then further extended to the reaction of $Na[Me_3Ga(L)]$ (L = pz or 3,5-Me_2pz) with chiral amino alcohols or aminothiols to yield compounds **106–109** [79]. No structural data are available for compounds **102–109**, however, the coordinating properties of these dimethylgalliumpyrazoyl alkoxides have been investigated. These compounds act as tridentate ligands to a range of transition metals, such as Cu [68a,71,72], Ni [68b], dinitrosyliron(I) [69], $M(CO)_3$ (M = Mn, Re and Mo) [70,72] and Rh(CO) or Rh(COMe)I [72,73]. Related complexes have also been isolated from the reaction of $Na[Me_3Ga(L)]$ (L = pz) with 2-pyridylmethanol (**110**) [74], 2-(dimethylaminomethyl)-3-hydroxypyridine (**111**) [75], 8-quinolinol (**112**) [75], *o*-aminophenol (**113**) [50] and 1-oxymethylpyrazoyl (**114**) [76]. Compounds **110–114** have also been shown to act as ligands to a range of transition metal species [50,74,75].



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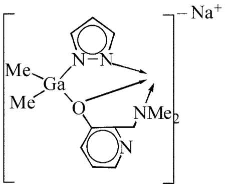

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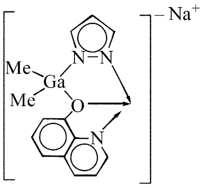

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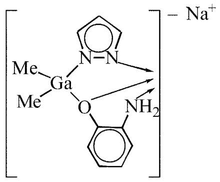

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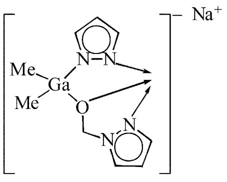


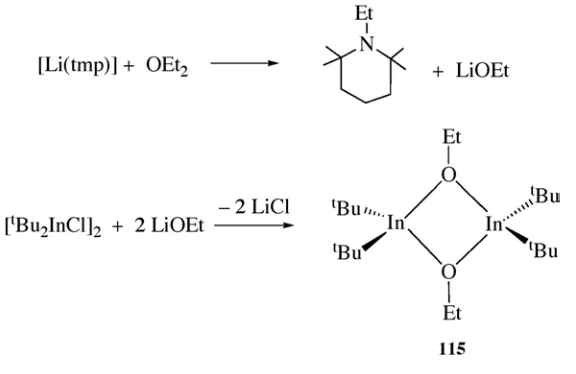
(114)

2.2. Indium(III)

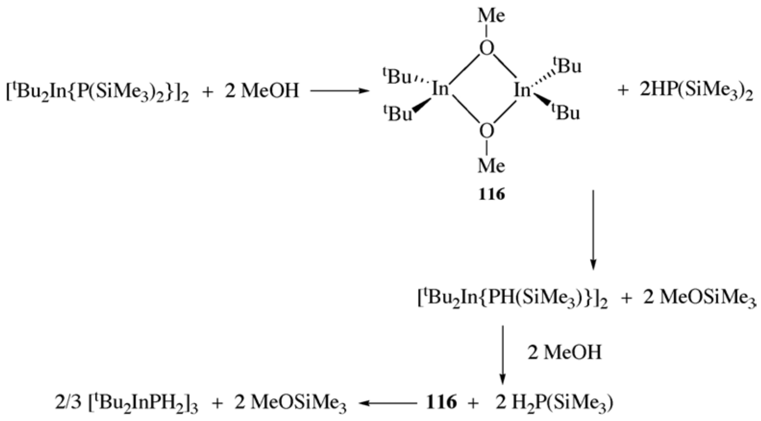
Early preparative routes to dialkylindium monoalkoxides involved the reaction of Me_3In with ROH, Eq. (1) [77,78]. The compounds $[R_2In(OR')]_n$ (R = Me, R′ = Me, CD_3, ${}^tBu$, $SiMe_3$; R = Et, R′ = Me, Et) were isolated and characterised [73–79]. The compounds $[{}^tBu_2In(OR)]_2$ (**115**, R = Et; **116**, R = Me) were subsequently reported and prepared using different synthetic procedures [80,81]. Salt elimination was used for the preparation of compound **115** via the reaction of $[{}^tBu_2InCl]_2$ with 2 equiv. of Li(tmp) in diethyl ether, as shown in Scheme 8. It was assumed that lithium ethoxide was produced from the reaction of Li(tmp) with diethyl ether.

In contrast, compound **116** was isolated from the reaction of $[{}^tBu_2In\{P(SiMe_3)_2\}]_2$ with methanol, with concomitant formation of $HP(SiMe_3)_2$, as depicted in Scheme 9. Interestingly, compound **116** reacted with the phosphine produced, $HP(SiMe_3)_2$, to yield $[{}^tBu_2In\{PH(SiMe_3)\}]_2$. The reaction of $[{}^tBu_2In\{PH(SiMe_3)\}]_2$ with 2 equiv. of methanol also afforded compound **116** or the trimer $[{}^tBu_2In(PH_2)]_3$ after longer reaction times. The structure of **115** and **116** have been determined, which showed that they are similar and compound **116** is isomorphous to its the gallium analogue (**11**) [22]. The In–O bond distances (**115**, 2.165(5) and 2.14(5) Å; **116**, 2.153(2) Å) and O–In–O angles (**115**, 75.2(2)°; **116**, 75.2(1)°) are comparable.

The compounds $[Me(Cl)InO^tBu]_2$ (**117**) and $[Me(Br)InO^tBu]_2$ (**118**) were synthesised via alcoholysis of the indium amide $[Me(X)In\{N(SiMe_3)_2\}]_n$ (X = Cl, Br), as shown in Scheme 10 [82]. Compound **117** was then reacted with $LiN(SiMe_3)_2$ to afford $[\{(Me_3Si)_2N\}MeInO^tBu]_2$ (**119**) with



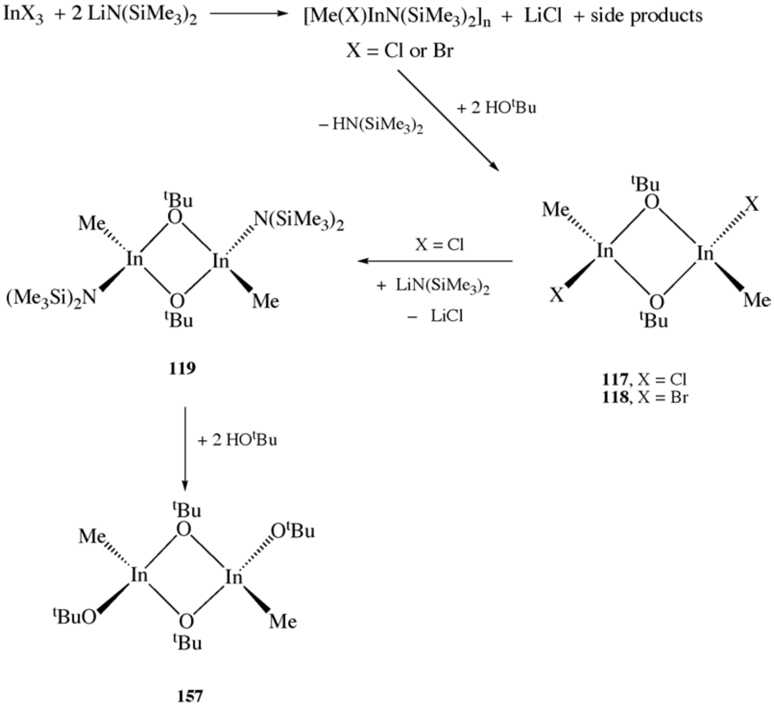
Scheme 8.



Scheme 9.

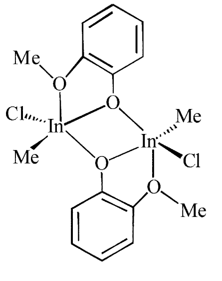
concomitant formation of LiCl. Compound **119** was used as a precursor to the formation of an indium bis(alkoxide) **157** (Section 3.2). The crystal structures of **117–119** indicate that they are all dimeric in the solid state. The In_2O_2 rings are planar with the oxygen atoms adopting a trigonal planar coordination and thus are sp^2-hybridised. The indium atoms adopt a distorted tetrahedral geometry in all the structures. The In–O bond lengths (**117**, 2.115(7) Å; **118**, 2.121(7) Å) are similar and shorter than those observed in compound **119** (2.1450(7) Å), probably due to the presence of the more electronegative halide group compared to a $N(SiMe_3)_2$.

The reaction between $[Me(Cl)In\{N(SiMe_3)_2\}]$ and the alcohol HOC_6H_4-2-OMe was also studied. The dimeric compound $[Me(Cl)InOC_6H_4\text{-2-OMe}]_2$ (**120**) was isolated and crystallographically characterised. The structure of **120** consists of a In_2O_2 ring, similar to compounds **117** and **118**. In addition, the structure of **120** contains two five-membered InO_2C_2 rings and two six-membered phenyl rings, all fused together. The In_2O_2 ring and phenyl rings are planar. However, the atoms within the InO_2C_2 rings are not equiplanar and deviate from planarity by 5°. The In–O(alkoxide) bond lengths are longer compared to **117** and **118** (2.204(4) Å) and the In–OMe bond distance (2.406(5) Å) is long. The related compound $[Me_2In(OC_6H_4CHO)]_2$ (**121**) has also been reported [83]. The structure of **121** was determined and revealed a dimeric molecule with a central In_2O_2 ring, two six-membered InO_2C_3 rings, and two phenyl groups all fused together. The O–In–O angles inside the In_2O_2 ring are larger

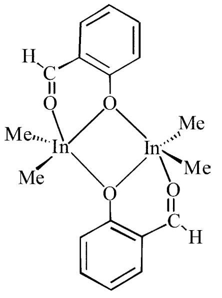


Scheme 10.

in **121** (74.8(1)°) than compared to **120** (70.3(2)°) and the In–O bond lengths (2.286(3) Å) longer.



120

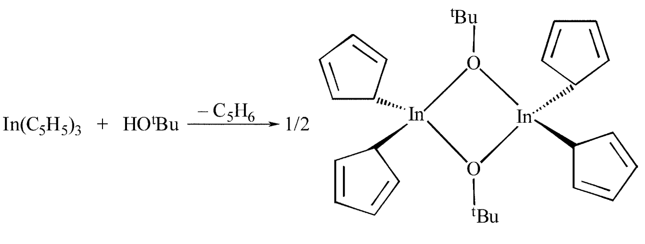


121

A novel approach for the generation of dialkylindium monoalkoxides has been reported recently [84]. Thus, the reaction [$R_2In(C_5H_5)$] with ^{t}BuOH resulted in the isolation of the compounds [$R_2In(O^tBu)]_2$ (R = Me (**116**), Me_3CCH_2 (**122**)), as shown in Eq. (10). The cyclopentadiene elimination reaction provided compounds **116** and **122** in nearly quantitative yield. Interestingly, no methane was evolved during the synthesis of **116**, even though Me_3In reacts with ^{t}BuOH to give **116**, as described above [80]. Unfortunately, X-ray quality crystals of **116** and **122** could not be obtained, although cryoscopic molecular weight determinations indicated that both compounds are dimeric. The related reaction between [$In(C_5H_5)_3$] and ^{t}BuOH yielded the dimeric compound [$(C_5H_5)_2In(O^tBu)]_2$ (**123**) (Eq. (11)) [85]. The dimeric nature of **123** was confirmed by X-ray diffraction and revealed that the indium centres adopt a distorted tetrahedral geometry (angle range from O–In–O 75.03(6)° to O–In–C 118.2(7)°). The In–O bond distances are 2.118(2) and 2.141(2) Å. The cyclopentadienide ligands are coordinated η^1 to the indium centre. There are intramolecular hydrogen bonding interactions between the C–H (from one CH_3 group of ^{t}Bu) and the cyclopentadienide rings. In addition, molecules of [$(C_5H_5)_2In(O^tBu)]_2$ form layers where molecules are connected by intermolecular H···π hydrogen bonds between the hydrogen atoms of a cyclopentadienide ligand and the π bonds of the cyclopentadienide ligand of the adjacent molecule. Treatment of $In(CH_2Ph)_3$ with dry O_2 afforded the related complex [$(PhCH_2)_2InOCH_2Ph]_2$ [86].

$$[R_2In(C_5H_5)] + {}^tBuOH \longrightarrow 1/2\,[R_2In(O^tBu)]_2 + C_5H_6 \qquad (10)$$

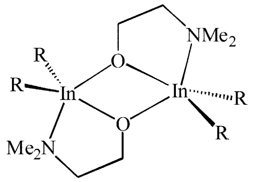
116, R = Me
122, R = Me_3CCH_2



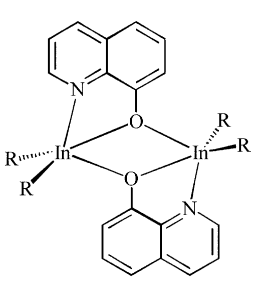
123

(11)

A number of dialkylindium alkoxides incorporating donor functionalised ligands have also been reported [87,88]. Reaction of R_3In with $HOCH_2CH_2NMe_2$ yielded the complexes [$R_2In(OCH_2CH_2NMe_2)]_2$ (**124**, R = Me; **125**, R = Et). Similarly, reaction of R_3In with 8-hydroxyquinoline afforded the compounds [$R_2In(Oquin)]_2$ (**126**, R = Me; **127**, R = Et). Molecular weight determinations suggested that compounds **126** and **127** are dimeric.

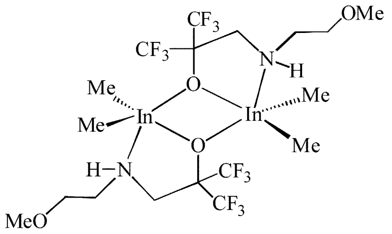


124, R = Me
125, R = Et

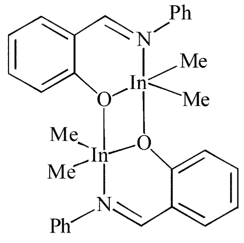


126, R = Me
127, R = Et

More recently, a series of dimethylindium aminoalkoxide complexes have been reported [88]. Treatment of Me_3In with $HOC(CF_3)_2CH_2NHR$ resulted in the formation of the dimeric complexes [$Me_2In(OC(CF_3)_2CH_2NHR)]_2$ (R = $(CH_2)_2OMe$ (**128**), Me (**129**) and ^{t}Bu (**130**)). In addition, the compound [$Me_2In(OC(CF_3)_2CH_2NMe_2)]_2$ (**131**) was isolated from the reaction between Me_3In and $HOC(CF_3)_2CH_2NMe_2$. For compounds **128–131** the existence of a dimeric In_2O_2 core structure in the solid state has been confirmed with the amino group located *trans* to the alkoxide ligands. VT-NMR studies of **129** showed that a rapid dimer-to-monomer equilibration and simultaneous breaking of N → In dative interaction occurs in solution. The structure of **128** has been determined and revealed a centrosymmetric, four-membered nearly planar In_2O_2 ring, common to this type of complex [82]. The structure of **128** is similar to the related gallium complexes such that the bridging alkoxide groups are located in both equatorial and axial positions while the nitrogen atom of the aminoalkoxide group is in the other axial position [54]. The In–O equatorial bond length of 2.2034(8) Å is significantly shorter than the In–O axial distance of 2.3959(8) Å.

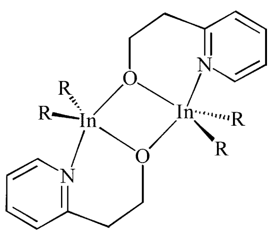


128



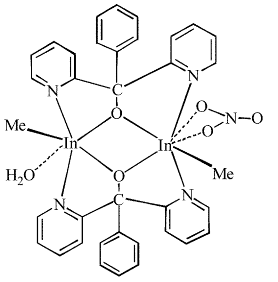
132

A dimeric intramolecularly coordinated indium complex was prepared from the reaction of Me_3In with the ligand *N*-phenylsaliclideneimine. The structure of compound **132** has been determined, which showed that it is dimeric with a planar In_2O_2 ring (O–In–O 74.51(11)°). The structure of **132** is in contrast to the gallium analogue (**82**), which is monomeric in the solid state. The geometry at the indium atom is distorted trigonal bipyramidal, as observed in related indium and gallium dimers. The In–O bond distances are significantly different at 2.158(3) and 2.477(3) Å, due to the geometry which dictates that each oxygen atom is in the equatorial position of one In atom and in the axial position for the other In atom. A related indium complex incorporating intramolecular alkoxide groups with pyridyl ligands has been reported [59]. The compounds $[R_2In(OCH_2CH_2(2\text{-}C_5H_4N)]_2$ (**133**, R = Me; **134**, R = Et) were synthesised from the reaction of R_3In with 2-(2-pyridyl)ethanol. The crystal structure of **133** was determined, which confirmed the dimeric nature of **133**. The structure of **133** is similar to **132** with O–In–O and In–O–In bond angles of 75.4(2)° and 104.6(2)° and In–O bond distances of 2.132(5) and 2.240(5) Å.

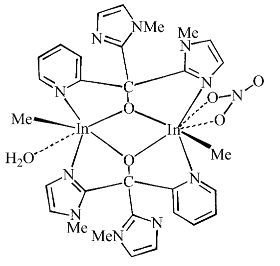


133, R = Me
134, R = Et

Reaction of $[Me_2In]NO_3$ with phenylbis(pyridin-2-yl)methanol $[(py)_2(Ph)COH]$, tris(pyridin-2-yl)methanol $[(py)_3COH]$, tris(*N*-methylimidazol-2-yl)methanol $[(mim)_3COH]$ and bis(*N*-methylimidazol-2-yl)(pyridin-2-yl)methanol $[(py)(mim)_2COH]$ resulted in the isolation of monomethylindium(III) complexes (**135–138**) containing binuclear cations [89,90]. The structures of two of these complexes have been determined (**135** and **138**). Each ligand has a pyridine group coordinated to one indium atom and a py or mim group coordinated to the other. Alkoxide bridges form a In_2O_2 kernel with In–O distances ranging from 2.165(6)–2.266(6) Å.

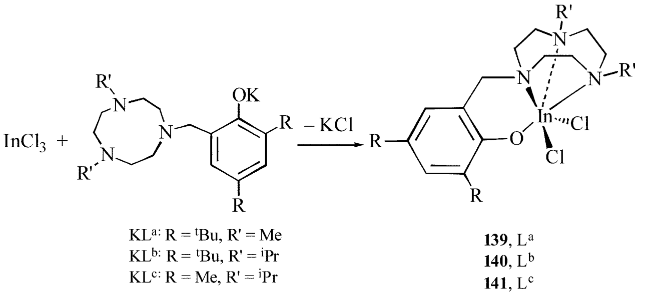


135 $[(InMe)_2\{\mu\text{-}(py)_2(Ph)CO\text{-}N,N',\mu\text{-}O\}_2(NO_3)(H_2O)]$



138 $[(InMe)_2\{\mu\text{-}(py)(mim)_2CO\text{-}N,N',\mu\text{-}O\}_2(NO_3)(H_2O)]$

The mono-pendant arm triazacyclononane indium complexes (**139–144**) have been reported recently, as shown in Eq. (12) [67,91]. The reaction of $KL^{a\text{–}c}$ with $InCl_3$ gave the monomeric derivatives $[In(\kappa^4\text{-}L^{a\text{–}c})Cl_2]$ (**139**, L^a, R = ^{t}Bu, R′ = Me; **140**, L^b, R = ^{t}Bu, R′ = ^{i}Pr; **141**, L^c, R = Me, R′ = ^{i}Pr). The crystal structure of $[In(\kappa^4\text{-}L^b)Cl_2]$ (**140**) revealed that the indium centre adopts a pseudo-octahedral geometry with the coordination sphere comprised of the κ^4-L^b group and two mutually *cis* chloride ligands. The In–O bond length in **140** is 2.076(5) Å. Related reactions of $In(CH_2Ph)_3$ with $HL^{a\text{–}c}$ resulted in the isolation of $[In(\kappa^4\text{-}L^a)(CH_2Ph)_2]$ (**142**), $[In(\kappa^2\text{-}L^b)(CH_2Ph)_2]$ (**143**) and $[In(\kappa^2\text{-}L^c)(CH_2Ph)_2]$ (**144**) [91]. Compounds **143** and **144** possess κ^2-bound ligands due to increased steric crowding with the N^{i}Pr ring than with the NMe derivatives.



KL^a: R = ^{t}Bu, R′ = Me
KL^b: R = ^{t}Bu, R′ = ^{i}Pr
KL^c: R = Me, R′ = ^{i}Pr

139, L^a
140, L^b
141, L^c

(12)

3. Bis(alkoxides) and (aryloxides)

Gallium and indium bis(alkoxide) compounds are rare species, in contrast to the well-known diorganoalkoxometallanes of these elements. As described in Section 2, reaction of a gallane or indane with an equimolar amount of alcohol affords the diorganoalkoxometallane complex, $[R_2MOR']_n$ in high yield. However, reaction of a gallane or indane with 2 equiv. or an excess of alcohol does not yield the expected gallium and indium bis(alkoxide) compounds, $[RM(OR')]_n$, in most cases. Instead reaction of Me_3M with an excess of alcohol often results in the formation of sesquialkoxides [12]. The synthesis and characterisation of the few examples of gallium and indium bis(alkoxide) complexes reported in the literature are described in Sections 3.1 and 3.2.

3.1. Gallium(III)

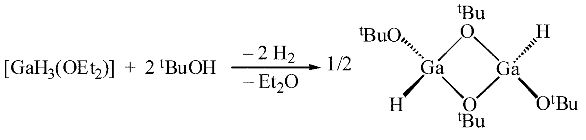
In 1968, Mehrotra and co-workers reported the preparation of gallium bis(alkoxides) via the reaction of gallium alkoxides, $[Ga(OR)_3]$ (Section 4.1) with acyl halides [92]. The reaction of $[Ga(OR)_3]$ with CH_3COX yielded $[Ga(OR)_2X]$ (**145**, R = ^{i}Pr, X = Cl; **146**, R = ^{i}Pr, X = Br; **147**, R = Et, X = Cl), as shown in Eq. (13). Compounds **145** and **146** were shown to be trimeric by molecular weight ebullioscopic measurements. In contrast, compound **147** showed dimeric behaviour in benzene solution.

$$[Ga(OR)_3] + MeCOX \longrightarrow [Ga(OR)_2X]_n + ROOCMe \quad (13)$$

145, R = ^{i}Pr, X = Cl
146, R = ^{i}Pr, X = Br
147, R = Et, X = Cl

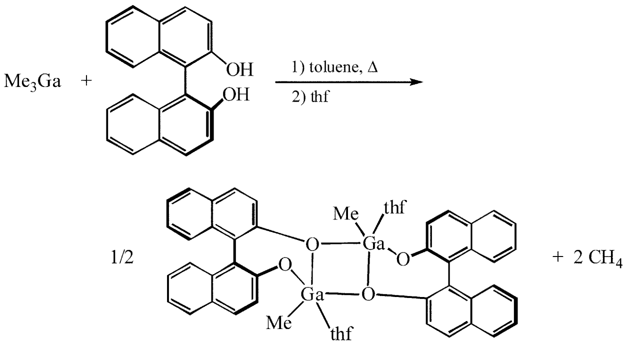
The only structurally characterised example of a gallium bis(alkoxide) incorporating a simple monodentate alkoxide group is the *tert*-butoxy compound $[HGa(O^tBu)_2]_2$ (**148**)

[36]. Compound **148** was synthesised by the 1:2 reaction of $[GaH_3(OEt_2)]$ and ^{t}BuOH in diethyl ether at 0 °C, followed by fractional sublimation or distillation under vacuum, as shown in Eq. (14). The ^{1}H and ^{13}C NMR spectra of **148** are complex due to the formation of a mixture of *cis* and *trans* isomers (*cis* and *trans* refer to the position of the hydrides with respect to the Ga_2O_2 central ring). The structure of **148** was determined and showed that the complex is dimeric with each gallium centre four-coordinate and approximately tetrahedral (terminal Ga–O 1.783(4) Å; av. bridging Ga–O 1.906(4) Å). The bridging oxygen atoms are in a trigonal planar environment.



148 (14)

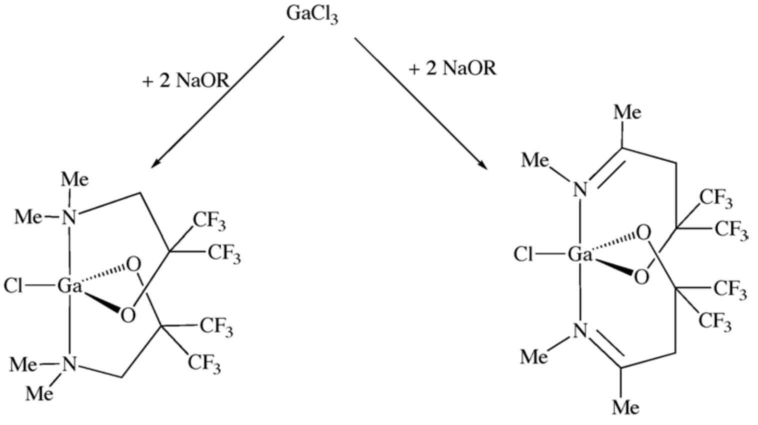
Reaction of Me_3Ga with 1 equiv. of the chelating ligand BINOL (2,2′-dihydroxy-1,1′-binaphthyl) at 105 °C, also resulted in the isolation of a dimeric gallium bis(alkoxide) (Eq. (15)) [93]. The initial poorly soluble white solid was suggested to comprise of a coordination polymer of the type $[MeGa((S)\text{-BINOLate})]_n$, which was recrystallised from THF to afford the dimer $[(THF)MeGa((S)\text{-BINOLate})]_2$ (**149**). X-ray crystallography showed that each gallium centre in **149** adopts a distorted trigonal bipyramidal geometry with the THF and O atom of one BINOLate ligand in the axial positions and the Cl atom and two bridging O atoms from the BINOLate ligands in equatorial positions (bridging Ga–O 2.072(4) Å; terminal Ga–O(BINOLate) 1.834(6) Å). The chelating and bridging BINOLate ligand results in a dihedral angle of 62° between the naphthyl groups.



149

(15)

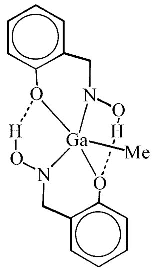
A mononuclear five-coordinate methyl gallium bis(salicylaldoximato-O^{1},*N*) complex (**150**) has been prepared from the reaction of Me_3Ga with salicylaldoxime [94]. X-ray diffraction showed that the gallium centre in **150** adopts a distorted square pyramidal geometry with the Ga atom displaced 0.7068(4) Å from the mean plane of the basal donor set towards the apical methyl carbon atom. The two salicylaldoxime ligands are linked by O–H···N hydrogen bonds between the NOH groups and the Ga–coordinated phenolic O atoms. The Ga–O and Ga–N bond lengths in **150** are 1.932(2) and 2.067(2) Å, respectively. The coordination chemistry of Ga(III) with 2-(2′-hydroxyphenyl)-2-benzoxazole (Hhbo) has also been studied [95]. Reaction of $[Ga(NO_3)_3\cdot xH_2O]$ with 3 equiv. of Hhbo and 3.3 equiv. of NaOAc yielded the compound $[Ga(hbo)_2(O,O'\text{-}CH_3CO_2)]$ (**151**). An X-ray structure determination confirmed the monomeric nature of **151** and showed that the gallium centre adopts a distorted octahedral geometry. The four O donor atoms define the equatorial plane and the Ga–O(hbo) bond distance of 1.873(2) Å is significantly shorter than the Ga–O(acetate) bond length of 2.117(2) Å.



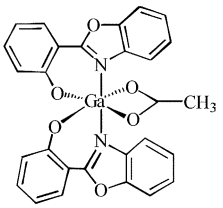
154, $R = C(CF_3)_2CH_2NMe_2$

155, $R = C(CF_3)_2CH_2C(CH_3){=}NMe$

Scheme 11.

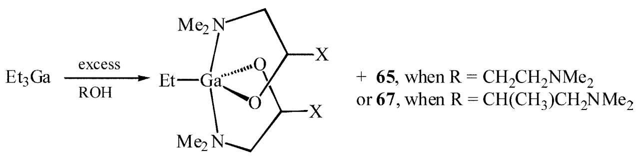


150



151

Recently, a monomeric gallium bis(alkoxide) incorporating donor functionalised ligands was reported [4]. Reaction of Et_3Ga with an excess of $HOCH_2CH_2NMe_2$ in refluxing toluene for 6 h, followed by sublimation, resulted in the isolation of a 1:1 mixture of $[Et_2Ga(OCH_2CH_2NMe_2)]_2$ (**65**) and the gallium bis(alkoxide) $[EtGa(OCH_2CH_2NMe_2)_2]$ (**152**), as shown in Eq. (16). Refluxing the reaction mixture for 24 h resulted in a 1:4 mixture of **65**:**152** [96]. The monomeric nature of **152** was confirmed by X-ray crystallography and showed that the gallium centre adopts a trigonal bipyramidal geometry, with the oxygen atoms of each alkoxide and an ethyl ligand occupying the three equatorial positions and the N atoms of the NMe_2 group in the axial positions. The Ga–O bond distances in **152** (1.8522(13) and 1.8534(13) Å) are comparable to the terminal Ga–O(alkoxide) bond length in **149**. The Ga–O–C bond angles of 117.3° and 117.7° suggest that there is little π-bonding between Ga and O in **152**. The mutually *trans* N-functionalities of the alkoxide ligand in **152** provide stability at the gallium centre via the donation of electron density into the same vacant Ga p-orbital. The related reaction between Et_3Ga and an excess of $HOCH(CH_3)CH_2NMe_2$ in refluxing toluene also resulted in the formation of a 1:1 mixture of $[Et_2Ga(OCH(CH_3)CH_2NMe_2)]_2$ (**67**) and the gallium bis(alkoxide) $[EtGa(OCH(CH_3)CH_2NMe_2)_2]$ (**153**), as identified by $^1H/^{13}C$ NMR and mass spectroscopy [4].



152, X = H
153, X = CH_3

(16)

Further examples of gallium bis(alkoxide) compounds incorporating donor-functionalised alkoxide groups were also reported recently, as shown in Scheme 11 [54]. Thus, reaction of $GaCl_3$ with 2.2 equiv. of NaOR resulted in the formation of the disubstituted compounds $[ClGa(OR)_2]$ (**154**, $R = C(CF_3)_2CH_2NMe_2$; **155**, $R = C(CF_3)_2CH_2C(CH_3){=}NMe$). The structures of **154** and **155** are similar to that previously reported of compound **152** [4], and a trigonal bipyramidal geometry is adopted at the monomeric Ga centre. In both **154** and **155**, the chloride and alkoxy groups occupy the equatorial positions and the nitrogen donors are located in the axial sites. The Ga–O and Ga–N bond distances in **154** and **155** are similar to those observed in compound **152**, although the Ga–N distances in **155** (2.087(2) and 2.092(2) Å) are shorter due to the formation of a stronger donor–acceptor bond for the imino N atom.

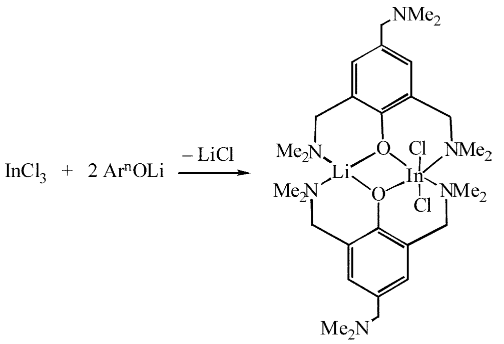
The ionic complex $Li[(Ar^nO)_2GaCl_2]$ (**156**) (Ar^n = 2,4,6-tris(dimethylamino-methyl)phenyl) was synthesised from the reaction of $GaCl_3$ with 2 equiv. of $LiOAr^n$ [53]. The gallate anion in **156** was observed in the CI(negative) mass spectrum. However, no structural data was reported although the indium analogue has been structurally characterised (Section 3.2).

3.2. Indium(III)

The only well-characterised example of an indium bis(alkoxide) incorporating a monodentate alkoxide is $[MeIn(O^tBu)_2]_2$ (**157**) [82]. Compound **157** was synthesised from amine/alcohol exchange via the reaction sequence outlined in Scheme 10. Initially, the amido complex $[Me(Cl)InN(SiMe_3)_2]_2$ was reacted with 2 equiv. of ^tBuOH to afford the indium mono(alkoxide) $[Me(Cl)InO^tBu]_2$ (**117**) (Section 2.2). Reaction of $LiN(SiMe_3)_2$ with **117** followed by ligand exchange with ^tBuOH resulted in the formation of $[MeIn(O^tBu)_2]_2$ (**157**). The solid-state structure of **157** comprises dimeric molecules with bridging alkoxide groups (In–O–In 103.6(2)°, O–In–O 76.4(2)°). The indium centre in **157** adopts a distorted tetrahedral coordination geometry with the In–O bond lengths to the terminal oxygen atoms being 0.12 Å shorter than the bond lengths in the In_2O_2 ring (bridging In–O 2.128(8) Å; terminal In–O 2.006(4) Å).

An indium bis(alkoxide) incorporating a donor functionalised ligand has been reported [97]. Reaction of $InCl_3$ with 2 equiv. of $Me_2NCH_2CH_2OLi$ afforded the compound $[ClIn(OCH_2CH_2NMe_2)_2]$ (**158**). No structural information was reported, however, compound **158** was shown to react with $Me_2Sn(CH_2Li)_2$ to yield the heterometallic alkoxide $[Me_2Sn(CH_2In(OCH_2CH_2NMe_2)_2]$.

The ionic compound $Li[(Ar^nO)_2InCl_2]$ (**159**) (Ar^n = 2,4,6-tris(dimethylamino-methyl)phenyl) was prepared in a similar manner to the gallium analogue (**156**) but using $InCl_3$ and $LiOAr^n$, as shown in Eq. (17) [53]. The crystal structure of **159** revealed that the indium centre adopts an octahedral coordination geometry with In–O bond lengths of 2.136(4) Å. A crystallographic C_2 axis passes through the indium and lithium atoms and the two Ar^nO ligands and the two chlorides are related by this C_2 axis. A planar InO_2Li ring results with the In and Li atoms bridged by two oxygen atoms.



159 (17)

4. Tris(alkoxides) and (aryloxides)

A number of synthetic routes for the formation of homoleptic gallium and indium alkoxides $[\mathrm{M(OR)_3}]$ (M = Ga, In) have been reported. The general procedures include reaction of the metal trihalide with NaOR, alcohol/alcohol exchange, amine/alcohol exchange and transesterification reactions. These general routes are shown in Eqs. (18)–(21).

$$\mathrm{MCl_3} + 3\mathrm{NaOR} \rightarrow [\mathrm{M(OR)_3}] + 3\mathrm{NaCl} \qquad (18)$$

$$[\mathrm{M(OR)_3}] + 3\mathrm{R'OH} \rightarrow [\mathrm{M(OR')_3}] + 3\mathrm{ROH} \qquad (19)$$

$$[\mathrm{M(OR)_3}] + 3\mathrm{MeCO_2R'} \rightarrow [\mathrm{M(OR')_3}] + 3\mathrm{MeCO_2R} \qquad (20)$$

$$[\mathrm{M(NR_2)_3}] + 3\mathrm{R'OH} \rightarrow [\mathrm{M(OR')_3}] + 3\mathrm{R_2NH} \qquad (21)$$

4.1. Gallium(III)

The first synthesis of homoleptic gallium alkoxide compounds $[\mathrm{Ga(OR)_3}]_n$ (R = alkyl) were reported in 1964 in separate papers by Mehrotra and Mehrotra [98] and Funk and Paul [99]. Thus, the reaction of $\mathrm{GaCl_3}$ with 3 equiv. of NaOR (Eq. (22)) resulted in the formation of gallium tris(ethoxide) (**160**) and gallium tris(isopropoxide) (**161**), respectively.

$$\mathrm{GaCl_3} + 3\ \mathrm{NaOR} \longrightarrow [\mathrm{Ga(OR)_3}] + 3\ \mathrm{NaCl}$$

160, R = Et
161, R = ^{i}Pr
(22)

A range of homoleptic gallium alkoxides were subsequently published and prepared via an alkoxide/alcohol exchange reaction (compounds **160–167**). Gallium tris(isopropoxide) was isolated from the reaction of $[\mathrm{Ga(OEt)_3}]$ and 3 equiv. of ^{i}PrOH, according to Eq. (23) [100]. In the same year, Funk and co-workers described the synthesis of $[\mathrm{Ga(OMe)_3}]$ and $[\mathrm{Ga(OEt)_3}]$ via exchange of the appropriate alcohol with $[\mathrm{Ga(OPh)_3}]$ [101].

$$[\mathrm{Ga(OR)_3}] + 3\ \mathrm{R'OH} \longrightarrow [\mathrm{Ga(OR')_3}] + 3\ \mathrm{ROH}$$

160, R = ^{i}Pr or Ph, R' = Et; **161**, R = Et, R' = ^{i}Pr;
162, R = ^{i}Pr or Ph, R' = Me; **163**, R = ^{i}Pr, R' = ^{n}Pr;
164, R = ^{i}Pr, R' = ^{n}Bu; **165**, R = ^{i}Pr, R' = ^{s}Bu;
166, R = ^{i}Pr, R' = ^{t}Bu
(23)

An extensive series of normal and branched gallium alkoxides were reported by Mehrotra and co-workers from the alcohol exchange reactions of $[\mathrm{Ga(O^{i}Pr)_3}]$ with ROH (R = Me, Et, ^{n}Pr, ^{n}Bu, ^{s}Bu and ^{t}Bu; compounds **160–166**) and transesterification reactions (compounds **161**, **163**, **164** and **166**) (see Eq. (24)) [102].

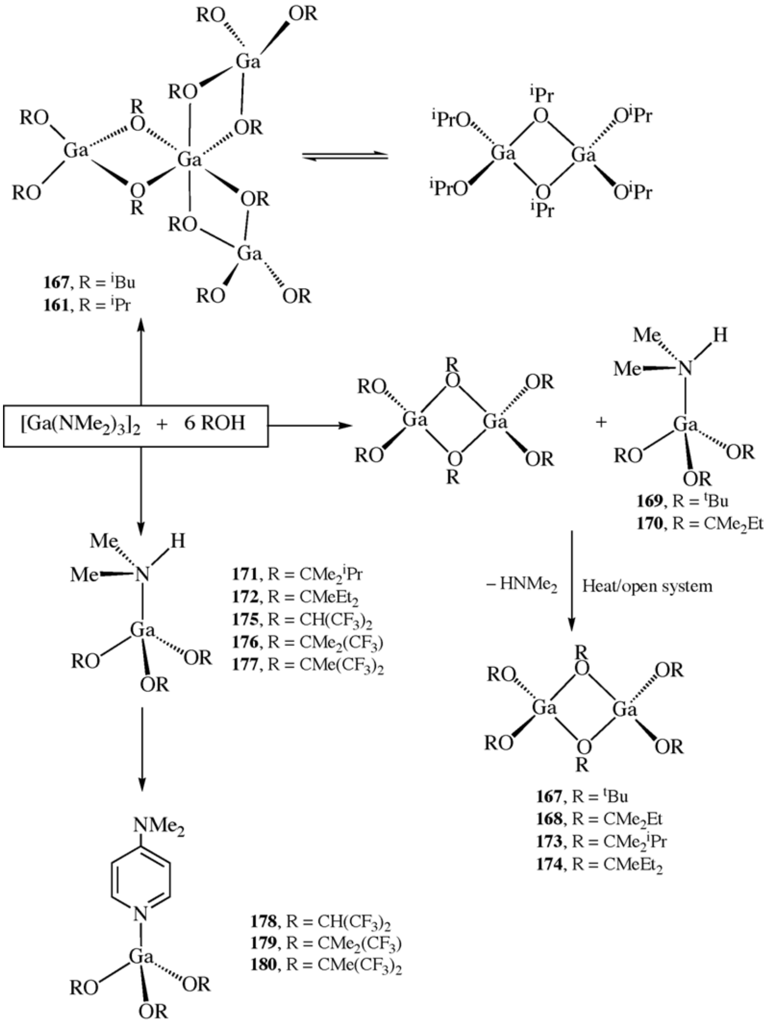
$$[\mathrm{Ga(OR)_3}] + 3\ \mathrm{MeCO_2R'} \longrightarrow [\mathrm{Ga(OR')_3}] + 3\ \mathrm{MeCO_2R}$$

R = Et or ^{i}Pr; **161**, R' = ^{i}Pr, **163**, ^{n}Pr **164**, ^{n}Bu **166**, ^{t}Bu
(24)

This series of compounds provided the first information regarding possible structures of the gallium tris(alkoxide) complexes. The ethoxide, propoxide and butoxide derivatives were proposed to be tetramers based on ebullioscopic molecular weight determinations. However, the isopropoxide and *t*-butoxide complexes were determined to be dimeric with the proposed structure $[\mathrm{Ga(\mu\text{-}OR)(OR)_2}]_2$. The dimer formulation for $[\mathrm{Ga(O^{t}Bu)_3}]_2$ was established using ^{1}H NMR spectroscopy [103]. Oliver and Worrall also demonstrated that $[\mathrm{Ga(O^{i}Pr)_3}]$ existed in solution as an equilibrium mixture of tetramer and dimer, as shown in Eq. (25) [104,105]. Furthermore, phase studies showed that gallium isopropoxide reacts with pyridine to form the 1:1 adduct $[\mathrm{Ga(O^{i}Pr)_3(py)}]$, as characterised by ^{1}H NMR and molecular weight studies [106].

$$\underset{\text{tetramer}}{\mathrm{Ga[(\mu\text{-}O^{i}Pr)_2Ga(O^{i}Pr)_2]_3}} \rightleftharpoons \underset{\text{dimer}}{2[\mathrm{Ga(\mu\text{-}O^{i}Pr)(O^{i}Pr)_2]_2}} \qquad (25)$$

Recently, a general synthetic procedure to gallium tris(alkoxide) compounds was reported, which involved amide/alcohol exchange via the reaction of gallium tris(dimethylamide) with alcohols, as shown Scheme 12 [5,6]. Reaction of $[\mathrm{Ga(NMe_2)_3}]_2$ with ^{t}BuOH and ^{i}PrOH resulted in the formation of the tetramers $\mathrm{Ga[(\mu\text{-}OR)_2Ga(OR)_2]_3}$, where R = ^{t}Bu (**167**) and ^{i}Pr (**161**), respectively [6]. The ^{1}H NMR spectra of **161** and **167** showed that the homoleptic gallium alkoxides were the only products formed. However, at room temperature in solution compound **161** evolved slowly into an equilibrium mixture of the tetramer and the dimer $[\mathrm{Ga(\mu\text{-}O^{i}Pr)(O^{i}Pr)_2}]_2$. These results were consistent with the earlier study by Oliver and Worrall [103]. Hoffman and co-workers also determined the thermodynamic parameters for the equilibrium (Scheme 12) and found that the formation of the dimeric product is entropy-driven. In addition, at room temperature the reactant tetramer is favoured slightly over the product dimers. In contrast, compound **167** showed no evidence for an analogous equilibrium even at elevated temperatures and only resonances arising from the tetramer was observed in the ^{1}H NMR spectra. The tetrameric structure of **161** was confirmed by an X-ray crystallographic study. Compound **161** consists of a six-coordinate central Ga atom surrounded by three four-coordinate Ga atoms. As such the structure of **161** is similar to the related tetramers $\mathrm{Al[(\mu\text{-}O^{i}Pr)_2Al(O^{i}Pr)_2]_3}$ [107] and $\mathrm{In[(\mu\text{-}OCHEt_2)_2In(OCHEt_2)_2]_3}$ [7].



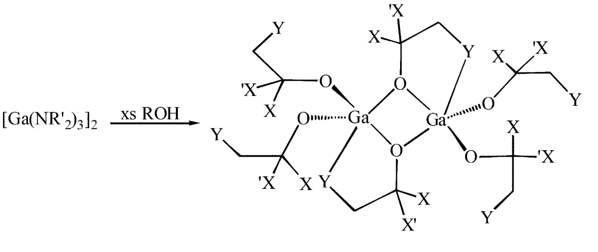
Scheme 12.

In contrast to the formation of the homoleptic gallium alkoxides **161** and **167**, the reaction of $[Ga(NMe_2)_3]_2$ with 6 equiv. of ^{t}BuOH or $EtMe_2COH$ afforded mixtures of $[Ga(\mu\text{-}OR)(OR)_2]_2$ (**166**, R = ^{t}Bu; **168**, R = CMe_2Et) and the amine adduct $[Ga(OR)_3(HNMe_2)]$ (**169**, R = ^{t}Bu; **170**, R = CMe_2Et) in 1:2 to 1:4 ratios, as shown in Scheme 12. However, similar reactions involving $^iPrMe_2COH$ and Et_2MeCOH formed $[Ga(OR)_3(HNMe_2)]$ (**171**, R = $CMe_2{}^iPr$; **172**, R = $CMeEt_2$) exclusively and no dimer formation was detected by ^{1}H NMR. The structure of $[Ga(\mu\text{-}OCMe_2Et)(OCMe_2Et)_2]_2$ (**168**) was reported and confirmed the dimeric nature of the complex. Compound **168** consists of a edge-shared tetrahedron structure common to dimeric group 13 alkoxide complexes. Homoleptic gallium alkoxide dimers $[Ga(\mu\text{-}OR)(OR)_2]_2$ (**166**, R = ^{t}Bu; **168**, R = CMe_2Et; **173**, R = $CMe_2{}^iPr$; **174**, R = $CMeEt_2$) were also obtained by heating the mixtures formed from the reaction of $[Ga(NMe_2)_3]_2$ with ROH or $[Ga(OR)_3(HNMe_2)]$ under dynamic vacuum (R = ^{t}Bu or CMe_2Et) or refluxing toluene solutions (R = $CMe_2{}^iPr$ or $CMeEt_2$). It was found that moderate heating of the solid (50 °C for 2–3 h) was necessary for sterically smaller R groups (^{t}Bu or CMe_2Et) whereas prolonged heating (toluene reflux for >2 days) was required when R was larger ($CMe_2{}^iPr$ or $CMeEt_2$). Thus, sterically demanding R groups favour retention of the amine ligand. An X-ray crystallographic study showed that $[Ga(O^tBu)_3(HNMe_2)]$ (**169**) consists of a four-coordinate Ga centre with a distorted tetrahedral geometry.

A range of related adducts incorporating fluoroalkoxide groups, of the type $[Ga(OR)_3(HNMe_2)]$ (**175**, R = $CH(CF_3)_2$; **176**, R = $CMe_2(CF_3)$; **177**, R = $CMe(CF_3)_2$) have also been prepared from the reaction of $[Ga(NMe_2)_3]_2$ and 6 equiv. of ROH (Scheme 12) [5]. Reaction of $[Ga(OR)_3(HNMe_2)]$ with 4-dimethylaminopyridine resulted in the formation of $[Ga(OR)_3(4\text{-}Me_2Npy)]$ (**178**, R = $CH(CF_3)_2$; **179**, R = $CMe_2(CF_3)$; **180**, R = $CMe(CF_3)_2$), as shown in Scheme 12. Crystal structure analysis showed that compounds **178** and **179** have a distorted tetrahedral geometry at the central Ga atom, similar to **169**. Interestingly, the dimethylaminopyridine ligand in **179** was not removed even after refluxing a toluene solution of **179** for 63 h.

Selected bond lengths and angles for compounds **161**, **168**, **169**, **178** and **179** are given in Table 1. There is little difference between the various angles in the tetrameric and dimeric complexes. In general, the trends in the M–$O_{terminal}$ and M–O_{bridge} (M = Al, Ga, In) distances in group 13 tris(alkoxides) follow the M^{3+} radii (Al^{3+} 0.57 Å; Ga^{3+} 0.62 Å; In^{3+} 0.92 Å [108]) such that M–O in the aluminium complexes are ~0.08 Å shorter than the corresponding gallium compounds, which are in turn around 0.2 Å shorter than the indium derivatives. A comparison of the Ga–N distances in the $[Ga(OR)_3L]$ (L = $HNMe_2$ or 4-Me_2Npy) complexes is not relevant due to the different donor abilities of the ligands and the presence of fluorinated substituents on some of the alkoxide groups, which changes the donor ability of the alkoxide ligand.

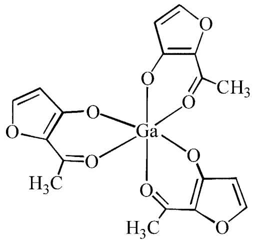
A range of gallium homoleptic alkoxides, of the type $[Ga(\mu\text{-}OR)(OR)_2]_2$, incorporating donor functionalised ligands (R = $CH_2CH_2NMe_2$, CH_2CH_2OMe, $CH(CH_3)CH_2NMe_2$, $C(CH_3)_2CH_2OMe$) have been reported recently [3,4]. Complexes of this type were synthesised in order to develop volatile precursors to gallium oxide (Section 5), which are less sensitive to air and moisture due to the stabilisation of the metal centre using the donor functionalised ligands [109]. Reaction of $[Ga(NMe_2)_3]_2$ and an excess of ROH resulted in the formation of $[Ga(\mu\text{-}OR)(OR)_2]_2$ (**181**, R = $CH_2CH_2NMe_2$; **182**, R = CH_2CH_2OMe; **183**, R = $CH(CH_3)CH_2NMe_2$; **184**, R = $C(CH_3)_2CH_2OMe$), as shown in Eq. (26) [4]. Compounds **181–184** were isolated as colourless oils and the dimeric nature was confirmed by mass spectroscopy. Infra-red spectroscopy also supported the dimeric structure of **181–184** with absorptions at ~557 and 538 cm^{-1}, corresponding to Ga_2O_2 ring modes. ^1H NMR indicated a fluxional coordination of the donor heteroatom with an absence of proton coupling in the alkoxide ligand and broadening of the associated resonances. The gallium alkoxides $[Ga(\mu\text{-}OR)(OR)_2]_2$ (**181**, R = $CH_2CH_2NMe_2$; **184**, R = CH_2CH_2OMe), have also been prepared by reaction of either $[Ga\{N(SiMe_3)_2\}_3]$ or $[Ga(NEt_2)_3]_2$ with ROH. The sterically encumbered gallium amide, $[Ga\{N(SiMe_3)_2\}_3]$, was less reactive than $[Ga(NEt_2)_3]_2$ and the reaction required refluxing in toluene for 6 h.



181: R' = Me, Et or $SiMe_3$, X = H, X' = H, Y = NMe_2
182: R' = Et or $SiMe_3$, X = H, X' = H, Y = OMe
183: R' = Me, X = CH_3, X' = H, Y = NMe_2
184: R' = Me, X = X' = CH_3, Y = OMe

(26)

Gallium tris(isomaltolato) (**185**) has been prepared via the reaction of $GaCl_3$ with the naturally occurring starch by-product isomaltol (Hima) in aqueous solution [110]. No structural data are available for **185**, however, analytical and spectroscopic data were consistent with a octahedral monomer. A series of related tris(ligand)gallium(III) complexes with 2-(2′-hydroxyphenyl)-2-oxazoline (Hoz), 2-(5′-bromo-2′-hydroxyphenyl)-2-oxazoline (Hbroz), 2-(2′-hydroxy-3′-methylphenyl)-2-oxazoline (Hmoz) and 2-(2′-hydroxy-3′-allylphenyl)-2-oxazoline (Haloz) have also been reported [111]. The complexes **186–189** were prepared by the reaction of $[Ga(NO_3)_3{\cdot}9H_2O]$ with the appropriate ligand in methanol/water in the presence of slightly greater than 3 equiv. of aqueous base (1 M NaOH). The structure of $[Ga(oz)_3]$ (**186**) and $[Ga(aloz)_3]$ (**189**) have been determined and showed that the gallium centres adopt a distorted octahedral coordination geometry. The bond lengths and angles in **186** and **189** are similar with the Ga–O distances in **186** ranging from 1.929(2) to 1.981(2) Å and in **189** from 1.920(3) to 1.938(2) Å.



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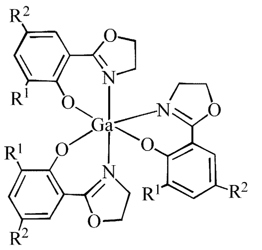


186, $R^1 = R^2 = H$
187, $R^1 = H$, $R^2 = Br$
188, $R^1 = Me$, $R^2 = H$
189, $R^1 = CH_2CH{=}CH_2$, $R^2 = H$

4.2. *Indium(III)*

Until recently the synthesis of homoleptic indium alkoxides was difficult and sometimes resulted in the formation of indium oxo-alkoxides. However, due to the interest in using homoleptic indium alkoxide compounds as precursors to indium oxide films, there has been increased research in this area. The synthesis of $[In(O^iPr_3)]_n$ (**190**) was first reported over 30 years ago by Mehrotra and co-workers [112]. Compound **190** was synthesised from the reaction of $InCl_3$ and 3 equiv. of NaO^iPr in refluxing 2-propanol (Eq. (27)) and was determined to have a molecular complexity of four in boiling 2-propanol.

$$InCl_3 + 3NaO^iPr \rightarrow \underset{\textbf{190}}{[In(O^iPr)_3]} + 3NaCl \qquad (27)$$

An extensive series of other indium tris(alkoxide) compounds $[In(OR)_3]_n$ were then prepared from **190** by alcohol/alkoxide exchange (R = Me (**191**), Et (**192**), ^{n}Bu (**193**), ^{s}Bu (**194**), pentyl (**195**)) or transesterification (**196**, R = ^{t}Bu), see Eqs. (28) and (29). The reaction between $InCl_3$ and NaO^iPr was later studied by Bradley and co-workers [113]. Employment of similar reaction conditions to those reported by Mehrotra et al. resulted in the formation of the oxo-centered cluster $[In_5(\mu_5\text{-}O)(\mu_3\text{-}O^iPr)_4(\mu_2\text{-}O^iPr)_4(O^iPr)_5]$

(**197**) rather than $[In(O^iPr)_3]$. Subsequent experiments by Bradley et al. suggested that the oxo group in the cluster was not the result of water contamination [114].

$$[In(O^iPr)_3] + 3\ ROH \longrightarrow [In(OR)_3] + 3\ ^iPrOH$$
$$R = Me\ \mathbf{191},\ Et\ \mathbf{192},\ ^nBu\ \mathbf{193},\ ^sBu\ \mathbf{194}\ \text{or pentyl}\ \mathbf{195} \quad (28)$$

$$[In(O^iPr)_3] + 3MeCO_2{}^tBu \rightarrow \underset{\mathbf{196}}{[In(O^tBu)_3]} + 3MeCO_2{}^iPr \quad (29)$$

Recently, a new synthetic route to indium tris(alkoxides) was developed and a number of structures reported [7,115,118]. The synthetic procedure involved the reaction of $[In\{N(^tBu)SiMe_3\}_3]$ [116] with the alcohols ^tBuOH, $EtMe_2COH$, Et_2MeCOH, $^iPrMe_2COH$ and $(CF_3)Me_2COH$, as depicted in Scheme 13 [7,118]. After work-up the dimers $[In(\mu\text{-}OR)(OR)_2]_2$ [$R = {}^tBu$ (**196**), CMe_2Et (**198**), $CMeEt_2$ (**199**), $CMe_2{}^iPr$ (**200**), $CMe_2(CF_3)$ (**201**)] or tetramer $In\{(\mu\text{-}CHEt_2)_2In(OCHEt_2)_2\}_3$ (**202**) were isolated. Compound **196** has also been prepared by reaction of $[In\{N(SiMe_3)_2\}_3]$ with *tert*-butanol in toluene [117]. Indium tris(isoproxide) (**190**) was prepared by the reaction of $[In\{N(^tBu)SiMe_3\}_3]$ with ^iPrOH or reaction of **196** with excess 2-propanol in benzene. All the compounds were very soluble in hexanes and benzene with the exception of **190**, which was found to be insoluble in a variety of solvents, including pyridine and hot 2-propanol. Therefore, compound **190** was proposed to be polymeric, $[In(O^iPr)_3]_n$ possibly with six-coordinate In centers. Interestingly, attempts to convert **190** into the previously reported oxo-alkoxide indium cluster $[In_5(\mu_5\text{-}O)(\mu_3\text{-}O^iPr)_4(\mu_2\text{-}O^iPr)_4(O^iPr)_5]$ (**197**) failed although similar reaction conditions were adopted.

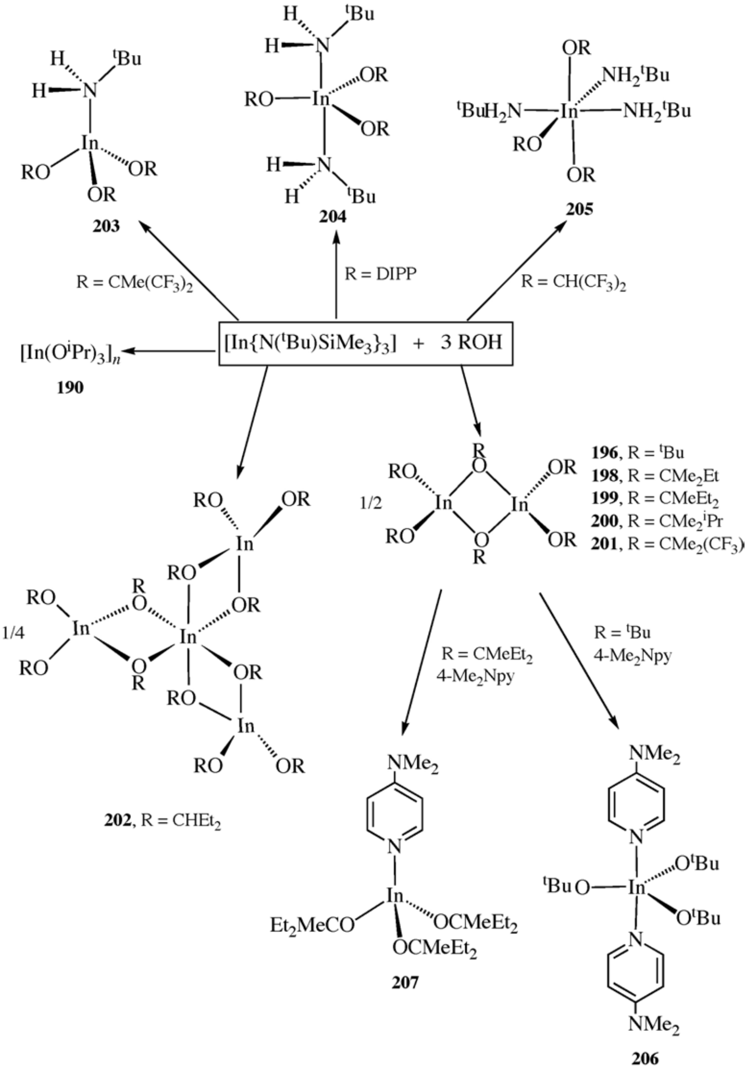
Related reactions between $[In\{N(^tBu)SiMe_3\}_3]$ and 3 equiv. of 2,6-diisopropylphenol, $(CF_3)_2MeCOH$ or $(CF_3)_2CHOH$ resulted in the formation of the *tert*-butylamine adducts $[In(OR)_3(H_2N^tBu)_n]$ [$n = 1$, $R = CMe(CF_3)_2$ (**203**); $n = 2$, $R = Dipp$ (**204**); $n = 3$, $R = CH(CF_3)_2$ (**205**)] [7,118]. The source of $^tBuNH_2$ was suggested to be the result of a secondary reaction between $^tBuNH(SiMe_3)$ and alcohol, as shown in Eq. (30). In order to avoid the generation of $^tBuNH_2$ in reactions between $[In\{N(^tBu)SiMe_3\}_3]$ and X–H reagents the lower limit on the $pK_a(X\text{–}H)$ was found to be approximately 10–11. Compounds **196** and **199** reacted with 1 or 2 equiv. of 4-dimethylaminopyridine to yield a five-coordinate $[In(O^tBu)_3(4\text{-}Me_2Npy)_2]$ (**206**) and four-coordinate $[In(OCMeEt_2)_3(4\text{-}Me_2Npy)]$ (**207**), respectively. The formation of **206** and **207** reflects the differences in size of the two alkoxide groups, with the bulkier alkoxide in **206** only coordinating one 4-dimethylaminopyridine ligand. Compound **196** was also reacted with 2,2,6,6-tetramethyl-3,5-heptadione ($^tBu_2$-β-diketone) in order to form a mixed alkoxide–acetoacetonate complex. The reaction resulted in the isolation of the complex $[(^tBuO)_2In(\mu\text{-}O^tBu)_2In(^tBu_2\text{-}\beta\text{-diketone})]$.

$$Me_3Si(^tBu)NH + ROH \rightleftharpoons {}^tBuNH_2 + ROSiMe_3 \quad (30)$$

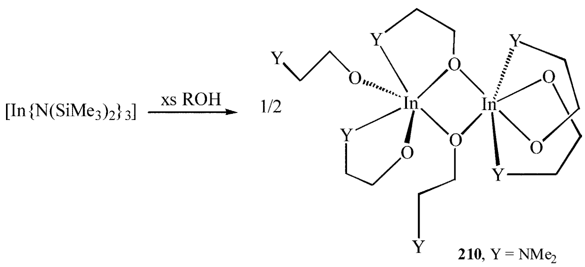
The indium amides, $[In(tmp)_3]$ and $[In(NEt_2)_3]$, were also investigated as precursors to indium alkoxides [7,118]. Reaction of $[In(tmp)_3]$ with 3 equiv. of $(CF_3)_2CHOH$ resulted in the isolation of the adduct $[In(OCH(CF_3)_2)_3(Htmp)]$ (**208**). Alternatively, compound **208** was synthesised from the reaction of $[In(tmp)_3]$ with 3 equiv. of $[H_2tmp][In(OCH(CF_3)_2)_4]$ with concomitant formation of Htmp. The pyridine adduct $[In(OCMe(CF_3)_2)_3(py)_3]$ (**209**) was prepared via the reaction of $[In(NEt_2)_3]$ with $(CF_3)_2MeCOH$ at 80 °C, followed by the addition of pyridine. Compound **209** was also synthesised via reaction of compound **203** with excess pyridine or addition of pyridine to the salt $[H_2tmp][In(OCMe(CF_3)_2)_4]$.

Crystal structures of $In[(\mu\text{-}OCHEt_2)_2(OCHEt_2)_2]_3$ (**202**), $[In(\mu\text{-}OR)(OR)_2]_2$ [$R = {}^tBu$ (**196**), $CMe_2(CF_3)$ (**201**)], $[In(OR)_3(L)]$ (**207**: $R = CMeEt_2$, $L = Me_2Npy$; **208**: $R = CH(CF_3)_2$, $L = Htmp$), $[In(OR)_3(L)_2]$ (**204**: $R = Dipp$, $L = H_2N^tBu$; **206**: $R = {}^tBu$, $L = Me_2Npy$), and $[In(OCMe(CF_3)_2)_3(py)_3]$ (**209**) have been reported [7,117,118]. The tetrameric complex $In[(\mu\text{-}OCHEt_2)_2(OCHEt_2)_2]_3$ (**202**), consists of central In atom, which is distorted from an octahedral geometry towards a trigonal prismatic geometry. The structure of **204** is similar to the gallium complex $Ga[(\mu\text{-}O^iPr)_2Ga(O^iPr)_2]_3$ (**161**) [6]. In the dimeric complexes **196** and **201**, the indium centers are four-coordinate and the In_2O_2 ring is slightly folded. Indium is four-coordinate in **207** and **208**, five-coordinate in **204** and **206** and six-coordinate in **209**. In compound **209** the central In atom adopts a *mer*-octahedral geometry whereas compound **207** has a distorted tetrahedral geometry and **208** a trigonal pyramidal with some distortion towards a tetrahedral geometry. Compounds **204** and **206** have trigonal bipyramidal geometries with the nitrogen ligand (H_2N^tBu in **204**; Me_2Npy in **206**) occupying the apical positions. For compound **204**, the angles in the trigonal plane span a wide range (99–139°, cf. compound **206** 117–125°) with a N–In–N angle of 177° (cf. 173° in **206**), due to the greater steric interactions around the *tert*-butyl substituents. The $In\text{–}OR_{terminal}$ and $In\text{–}OR_{bridging}$ distances in the abovementioned structures are not unusual, and selected bond lengths and angles are presented in Table 1.

Donor-functionalised indium alkoxides, $[In(OR)_3]_2$ (**210**, $R = CH_2CH_2OMe$; **211**, $R = CH_2CH_2NMe_2$) have been prepared by alcoholysis of $[In\{N(SiMe_3)_2\}_3]$ [119] according to Eq. (31). An X-ray crystallographic study of **211** shows that in the solid state the unsymmetrical $[In(\mu,\eta^1\text{-}OR)(\mu,\eta^2\text{-}OR)(\eta^2\text{-}OR)_3(\eta^1\text{-}OR)]$ ($R = CH_2CH_2NMe_2$) dimeric structure is adopted with two $[InO_6]$ octahedra sharing a common edge. The In–O bond distances (2.056(4)–2.189(4) Å) are longer than for alkoxides where indium is only four-coordinate. The In–N bond distances (2.324(6)–2.477(5) Å) are in the range observed for In–N coordination bonds [7].

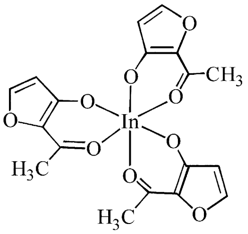


Scheme 13.



210, Y = NMe$_2$
211, Y = OMe (31)

Indium tris(isomaltolato) (**212**) has been synthesised from the reaction of In(NO$_3$)$_3$·5H$_2$O and 3 equiv. of isomaltol (Hima) in aqueous solution [110]. No structural data are available for **212**, however, analytical and spectroscopic data are consistent with a octahedral monomer. The indium analogues of the gallium complexes **186–189** have been prepared from the reaction of In(NO$_3$)$_3$·5H$_2$O with 2-(2′-hydroxyphenyl)-2-oxazoline (Hoz), 2-(5′-bromo-2′-hydroxyphenyl)-2-oxazoline (Hbroz), 2-(2′-hydroxy-3′-methylphenyl)-2-oxazoline (Hmoz) and 2-(2′-hydroxy-3′-allylphenyl)-2-oxazoline (Haloz) [111]. The complexes **213–216** were prepared by the reaction of In(NO$_3$)$_3$·5H$_2$O with the appropriate ligand in methanol/water in the presence of slightly greater than 3 equiv. of aqueous base (1 M NaOH). The structure of [In(oz)$_3$] (**215**) was determined and showed that the indium centre adopts a distorted octahedral coordination geometry. The In–O bond lengths in **215** range from 2.103(2) to 2.149(3) Å.



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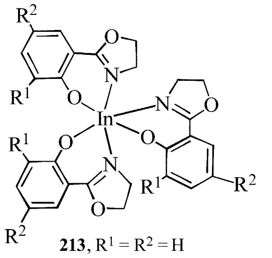

213, R^1 = R^2 = H
214, R^1 = H, R^2 = Br
215, R^1 = Me, R^2 = H
216, R^1 = CH$_2$CH=CH$_2$, R^2 = H

5. Applications of gallium(III) and indium(III) alkoxides

In recent years, there has been increasing interest in the synthesis of new gallium and indium alkoxide complexes because of their potential use as precursors for the production of gallium and indium oxide films by CVD. Gallium oxide (Ga_2O_3) films have recently attracted interest due to their application as high-temperature gas sensors [120,121]. Indium oxide films are conductive and transparent to visible light and could be suitable for applications such as solid-state optoelectronic devices [7]. The gallium alkoxide complexes $[Ga(OCH(CF_3)_2)_3(HNMe_2)]$ (**175**), $[Ga(\mu\text{-}O^tBu)(O^tBu)_2]_2$ (**167**), $[Me_2Ga(OC(CF_3)_2CH_2NMe_2)]$ (**81**), $[ClGa(OC(CF_3)_2CH_2NMe_2)_2]$ (**154**), $[Et_2Ga(OCH_2CH_2NMe_2)]_2$ (**65**) and $[Et_2Ga(OC(CH_3)_2CH_2OMe)]_2$ (**68**) have all been used to prepare Ga_2O_3 thin films by CVD [4–7,54]. Gallium oxide films were prepared from compound **175** and air by low-pressure (LP)CVD at 250–450 °C [5]. Good quality films were obtained at 450 °C, which were shown to have the composition $Ga_2O_{3.1}$ with an optical band gap of 4.9 eV. The Ga_2O_3 film was amorphous, as shown by powder X-ray diffraction. Interestingly, attempted depositions using only compound **175** (no air) or in combination with dry O_2 did not afford films in the same temperature range. This suggests that water vapour is the critical reactant in the **175**/air precursor system.

LPCVD of $[Ga(\mu\text{-}O^tBu)(O^tBu)_2]_2$ (**167**) and O_2 also resulted in the formation of Ga_2O_3 [6]. Films were grown at 300–700 °C and were highly transparent. In contrast to **175**, a film of good quality was also produced from compound **167** at 400 °C without added air or O_2. The films were shown to be of composition Ga_2O_3 and amorphous. However, a film annealed at 1000 °C produced an X-ray pattern consistent with polycrystalline $\beta\text{-}Ga_2O_3$. Gallium oxide (Ga_2O_3) deposition was also achieved using the compounds $[Me_2Ga(OC(CF_3)_2CH_2NMe_2)]$ (**81**) and $[ClGa(OC(CF_3)_2CH_2NMe_2)_2]$ (**154**) with high-purity O_2 as the carrier gas at 500–600 °C [54]. The films were fluorine- and chlorine-free but showed 3–5 atom% carbon impurity. The related complexes $[Et_2Ga(OCH_2CH_2NMe_2)]_2$ (**65**) and $[Et_2Ga(OC(CH_3)_2CH_2OMe)]_2$ (**68**) were used alone and formed carbon-contaminated gallium oxide films under LPCVD at 600 °C [4]. However, annealing at 900 °C under air produced highly crystalline $\beta\text{-}Ga_2O_3$ films.

Good quality In_2O_3 films have been deposited from $[In(\mu\text{-}OCMe_2Et)(OCMe_2Et)_2]_2$ (**198**), $[In(OCMe(CF_3)_2)_3(H_2N^tBu)]$ (**203**) and $[Me_2In(OC(CF_3)_2CH_2NHMe)]_2$ (**129**) [7,118,88]. LPCVD of **198** and O_2 afforded highly conductive indium oxide films at 300–500 °C. Analysis showed that the film deposited at 500 °C was stoichiometric In_2O_3 and X-ray diffraction indicated (1 0 0)-orientated cubic indium oxide. Polycrystalline indium oxide (In_2O_3) films were deposited from $[In(OCMe(CF_3)_2)_3(H_2N^tBu)]$ (**203**) and O_2 at 400–550 °C via LPCVD. Films deposited below 500 °C contained 2–3 atom% fluorine whereas the film deposited at 550 °C had no detectable fluorine. X-ray diffraction studies on films grown at 400–550 °C indicated that they were polycrystalline cubic indium oxide with a (1 0 0) preferred orientation. Similar results were obtained from the LPCVD of $[Me_2In(OC(CF_3)_2CH_2NHMe)]_2$ (**129**) with O_2 at 400–500 °C. However, powder X-ray diffraction showed the formation of cubic In_2O_3 films with preferred (1 1 1)-orientation.

The homoleptic gallium alkoxide $[Ga(OCH_2CH_2OMe)_3]_2$ (**183**) has been used for the preparation of $[ZnGa_2(OCH_2CH_2OMe)_8]_2$ [3]. The heterometallic alkoxide, $[ZnGa_2(OCH_2CH_2OMe)_8]_2$ was then used in sol–gel processing to produce crystalline $ZnGa_2O_4$.

A range of dialkylgallium alkoxides incorporating donor functionalised ligands have been assessed for their use in organic synthesis [1,2,47,122]. The compounds $[Me_2Ga(OR)]_2$ ($R = CH_2CH_2NMe_2$ (**49**), CH_2CH_2OMe (**53**), $OC_6H_4\text{-}2\text{-}OMe$ (**71**)) have been shown to methylate aryl and vinyl bromides and iodides in a selective manner in the presence of a palladium catalyst [1,2,122]. The substituted bromobenzenes XC_6H_4Br (X = CHO, COPh, CO_2Et, CN, NO_2, Cl, CH_2Br, CH=CHCOPh) could be methylated by compounds **49**, **53** and **71** at the aromatic ring halogen atom to give substituted toluenes as single products. The methylated rates depended on the nature of the chelating ligand, the solvent and the type of palladium catalysts employed. Similarly, the cross-alkylation of a range of naphthyl halides and triflates has been achieved in the presence of compound **53** and a palladium catalyst [47]. The intramolecularly stabilised gallium and indium complexes $[Me_2M(CH_2CH_2OMe)]_2$ have been shown to cross-couple with a variety of chloroarenes in the presence of $[NiCl_2(PPh_3)_2]$ to yield the respective alkylated arenes, selectively [123].

6. Conclusions

The synthesis and structures of gallium and indium alkoxides reported to date have been described in this review. The dialkylgallium monoalkoxides represent the majority of the gallium and indium alkoxides reported thus far. However, the chemistry of gallium and indium tris(alkoxides), and to a lesser extent the bis(alkoxides) has been extended recently. In general, the trends in the $M\text{–}O_{terminal}$ and $M\text{–}O_{bridge}$ (M = Al, Ga, In) distances in group 13 alkoxides follow the M^{3+} radii (Al^{3+} 0.57 Å; Ga^{3+} 0.62 Å; In^{3+} 0.92 Å [108]) such that M–O in the aluminium complexes are ∼0.08 Å shorter than the corresponding gallium compounds, which are in turn around 0.2 Å shorter than the indium derivatives.

The gallium and indium tris(alkoxides) have been shown to act as excellent precursors to metal oxides. These compounds are able to decompose and form metal oxide thin films under CVD conditions at relatively low temperatures. Furthermore, little contamination from other species (e.g. carbon or fluorine) was observed in the resulting materials. Preliminary studies have also shown that these complexes can be used to form ternary materials and may find application in organic synthesis

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