ELSEVIER

Coordination Chemistry Reviews
223 (2001) 217–264

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Amido compounds of gallium and indium

Claire J. Carmalt

Department of Chemistry, University College London, Christopher Ingold Laboratories,
20 Gordon Street, London WC1H 0AJ, UK

Received 10 November 2000; accepted 15 March 2001

Contents

Abstract

This article presents a systematic and extensive review of the syntheses, structures and reactivities of amido compounds of gallium and indium. Mono-, di- and triamides have been synthesised and structurally characterised for both gallium and indium. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Gallium amides; Indium amides; Synthesis

---

* Tel.: +44-207-679-7528; fax: +44-207-679-7463.
E-mail address: c.j.carmalt@ucl.ac.uk (C.J. Carmalt).

PII: S0010-8545(01)00385-X

1. Introduction

One of the driving forces for the continued interest in nitrogen containing compounds of the Group 13 elements relates to their use as single-source precursors to the technologically important Group 13 nitride semiconductors, MN (M = Al, Ga, In) [1]. The majority of the known amido complexes of gallium and indium are of type $[R_2M–NR'_2]$ and feature a 1:1 stoichiometry. These complexes are characterised by a marked tendency to oligomerise through the formation of strong metal–nitrogen bridges. Monomeric amido derivatives can be stabilised by the presence of bulky substituents on the Group 13 and nitrogen atoms. From the standpoint of nitride precursor chemistry, monomers are thought to be favoured over dimers or higher oligomers because of their increased volatility and potentially simple deposition process. Monomers are also important because the metals are coordinatively unsaturated and the nitrogen centres possess lone pairs that are not involved in bonding. These lone pairs are therefore available to interact with the formally empty p-orbitals on the metal to form π-bonds. However, efficient delocalisation requires planar geometry at both atoms and the alignment of their coordination planes. These conditions are difficult to achieve, as discussed recently in a number of reviews [2a,2b].

Recently, there has been a discernible shift in interest towards the heavier elements in Group 13 and this review will concentrate on gallium and indium amido complexes. Organoamides of aluminium have been reviewed recently [3]. Previous reviews [2,4] have covered some aspects of amido 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–N bond lengths, M···M distances, N–M–N and M–N–N bond angles, and torsion angles) for selected examples of gallium and indium amido complexes are presented in Table 1.

The following abbreviations will be used: 1-Ad = 1-Adamantanyl; NHBp = 2-aminobiphenyl; Cp* = pentamethylcyclopentadienyl; Cy = cyclohexyl; Dipp = 2,6-diisopropylphenyl ($–C_6H_3$-2,6-^{i}Pr$_2$); dmf = dimethylformamide; dmp = 2,6-dimethylpiperidinato; Mes = mesityl (2,4,6-trimethylphenyl or $–C_6H_2$-2,4,6-Me$_3$); Mes* = 2,4,6-tri-*tert*-butylphenyl or $–C_6H_2$-2,4,6-^{t}Bu$_3$; Np = naphthyl; pip = piperidinato; py = pyridine; pyrr = pyrrole; pz = pyrazolyl; quin = quinuclidine; thf = tetrahydrofuran; tmp = 2,2,6,6-tetramethylpiperinato; Trip = 2,4,6-triisopropylphenyl ($–C_6H_2$-2,4,6-^{i}Pr$_3$); Xyl = $–C_6H_3$-2,6-Me$_2$.

2. Monoamides

Various methods have been used to synthesise monoamides of gallium and indium, the most common being the reaction of organometallic halide complexes $[R_2MX]$ or $[RMX_2]$ (R = alkyl or aryl, M = Ga or In, X = halide) with early main group reagents (e.g. LiN(R′)R″ or NaN(R′)R″), for example Eqs. (1) and (2). Transmetallation of gallium and indium halides (MX_3) with lithium disilylamides has also been employed in the synthesis of these complexes.

Table 1
Selected bond lengths and angles for gallium and indium amides

No.	Compound	Framework	Bond length (Å)	Bond angles (°)		Bond length (Å)	Torsion angle (°) †	References
			M–N(amido)	N–M–N	M–N–M	M···M (Å)		
Gallium monoamides								
Trimeric								
1	$[H_2Ga\overline{NCH_2C}H_2]_3$	Ga_3N_3 ring, chair	1.97(9) (av)	100	116			[5,6]
2	$[H_2GaNH_2]_3$	Ga_3N_3 ring, chair	1.981(4) (av)	100.3(5)	117.1(3) (av)			[7,8]
102	$[Me_2GaNH_2]_3$	Ga_3N_3 ring, ‘sofa’	1.99(2) (av)	98.5 (av)	122.2 (av)	3.446 (av)		[51]
101	$[{}^tBu_2GaNH_2]_3$	Ga_3N_3 ring, planar	2.017(2)	106.4(1)	134.5(3)	3.719(3)		[50]
Dimeric								
107	$[\eta^1\text{-}Cp^*Ga(\mu\text{-}N_3)\{N(SiMe_3)_2\}]_2$	Ga_2N_2 ring, planar	$1.872(2)^t$	–	–			[55]
86	$[MeGaNPh_2]_2(\mu\text{-}NPhC_6H_4)$	Ga_2N_2 ring, folded	$1.892(3)^t$ $2.053(1)^{br}$	84.97 (av)	84.80 (av)	2.7686(8)		[40b]
9	$[Cl_2GaN(H)SiMe_3]_2$	Ga_2N_2 ring, planar	1.969(4) (av)	90.0 (av)	90.0	2.810(1)		[15]
13	$[Cl_2GaN(Me)SiMe_3]_2$	Ga_2N_2 ring, planar	1.986(5) (av)	90.0 (av)	90.0 (av)	2.809		[15]
84	$[Me_2Ga(NCMe_2)]_2$	Ga_2N_2 ring, planar	1.989(4) (av)	82.1	97.9			[48]
10	$[Br_2GaN(H)SiMe_3]_2$	Ga_2N_2 ring, planar	2.000(18)	89.6(7)	90.4(7)	2.832(5)		[16]
14	$[\{Me_2GaNHSiMe_3\}Me_2GaCl]$	GaNGaCl ring, folded	2.000(3)	–	–			[14]
48	$[Mes(Cl)GaN(H){}^tBu]_2$	Ga_2N_2 ring, planar	2.002(7) (av)	85.3(3)	94.7	2.944(2)		[33]
56	$[Cy_2GaN(H){}^tBu]_2$	Ga_2N_2 ring, planar	2.01(7) (av)	84.6(6)	96.5(2)	3.017(3)		[35b]
6	$[Me(Cl)GaN(H)SiMe_3]_2$	Ga_2N_2 ring, planar	2.012(8)	89.0	91.0	2.870(2)		[13]
54	$[Me_2GaN(H){}^tBu]_2$	Ga_2N_2 ring, planar	2.012(4)	85.0 (av)	95.0 (av)	2.9755		[35a,42]
4	$[H_2GaNEt_2]_2$	Ga_2N_2 ring, planar	2.017	90.1(2)	89.9(2)	2.845(2)		[10]
89	$[Me\overline{Ga\text{-}\{\mu\text{-}NHC_6H_2Me_2\text{-}4,6,13,15\text{-}C}H_2\text{-}2,11\}_2GaMe_2$	Ga_2N_2 ring, slightly folded	2.013 (av)	87.9(4)	92.0(4)			[40a]
85	$[Me\overline{GaN(CH_2C}_6H_4)(CH_2Ph)]_2$	Ga_2N_2 ring, planar	2.018(3) 2.045(3)	90.1(7)	89.3(1)	2.854		[34b]
68	$[(PhMe_2CCH_2)_2GaN(H){}^nPr]_2$	Ga_2N_2 ring, planar	2.021(2) (av)	86.7(1)	93.3(1)	2.938(1)		[44a]
88	$[Me\overline{Ga\{\mu\text{-}NHC_6H_2Me_2\text{-}4,6\text{-}C}H_2\text{-}2\}]_2$	Ga_2N_2 ring, planar	2.023 (av)	87.7(2)	92.3(4)	2.918		[40a]
65	$[Me_2GaN(H)Dipp]_2$	Ga_2N_2 ring, folded	2.024(1) (av)	83.6(4)	94.2(4)	2.998		[40a]

Table 1 (*Continued*)

No.	Compound	Framework	Bond length (Å)	Bond angles (°)		Bond length (Å)	Torsion angle (°) †	References
			M–N(amido)	N–M–N	M–N–M	M···M (Å)		
87	$[\mathrm{Me}\overline{\mathrm{Ga}\{\mu\text{-}\mathrm{NHC_6H_3}\text{-}{}^i\mathrm{Pr}\text{-}6\text{-}\mathrm{CMeHC}}\mathrm{H_2}\text{-}2\}]_2$	Ga_2N_2 ring, planar	2.025(4) (av)	86.4(2)	93.7(2)	2.97		[40a]
3	$[\mathrm{H_2GaNMe_2}]_2$	Ga_2N_2 ring, planar	2.027(4) (av)		90.6	2.881		[5,10]
15	$[\mathrm{Me_2Ga\{NHSiEt_3\}}]_2$	Ga_2N_2 ring, planar	2.029(4) (av)	88.2(2)	91.2(2)	2.915(2)		[20]
66	$[\mathrm{Me_2GaN(H)1\text{-}Ad}]_2$	Ga_2N_2 ring, folded	2.031(3)	85.3(1)	94.7(1)	2.977		[40a]
			2.037(5)	85.2(2)	94.8(2)	2.973		[41]
62	$[\mathrm{Me_2Ga}\overline{\mathrm{N(CH_2)_2N(Me)CH_2C}}\mathrm{H_2}]_2$	Ga_2N_2 ring, planar	2.032(2) (av)	87.6(1)	92.4(1)	2.932(1)		[34a]
20	$[\mathrm{Me_2GaN(^iPr)SnMe_3}]_2$	Ga_2N_2 ring, planar	2.035(4) (av)	89.3(2)	90.7(2)	2.892(1)		[22,23]
57	$[\mathrm{Cy_2GaN(H)Ph}]_2$	Ga_2N_2 ring, planar	2.038(7) (av)	84.4(3)	95.4(6)			[35b]
49	$[\mathrm{^iPr_2GaN(H)^tBu}]_2$	Ga_2N_2 ring, planar	2.039(3) (av)	84.8(1)	95.2(1)	3.010(9)		[33]
67	$[\mathrm{Me_2GaN(H)Ph}]_2$	Ga_2N_2 ring, planar	2.039(3)	86.4(1)	93.6(1)	2.972		[40a]
52	$[\mathrm{Me_2GaN(CH_2Ph)_2}]_2$	Ga_2N_2 ring, slightly folded	2.044(6) (av)	90.0	89.9	2.887(2)		[34a]
19	$[\mathrm{Me_2GaN(^nPr)SnMe_3}]_2$	Ga_2N_2 ring, planar	2.045(5)	88.9(2)	91.1(2)			[22]
92	$[\mathrm{(PhMe_2CCH_2)_2GaN(H)^tBu}]_2$	Ga_2N_2 ring, planar	2.050(3) (av)	84.2(1)	95.8(1)	3.044(1)		[44c]
24	$[\mathrm{Et_2GaN(^iBu)_2}]_2$	Ga_2N_2 ring, folded	2.054(6) (av)	87.4	88.4	2.864(1)		[23]
70	$[\mathrm{(PhMe_2CCH_2)_2GaN(H)Ph}]_2$	Ga_2N_2 ring, planar	2.055(4) (av)	85.7 (av)	94.3 (av)	3.013		[44b]
58	$[\mathrm{^tBu_2GaN(H)Ph}]_2$	Ga_2N_2 ring, planar	2.06(4) (av)	83.5(3)	96.5(2)			[35c]
55	$[\mathrm{^tBu_2GaN(H)^tBu}]_2$	Ga_2N_2 ring, planar	2.064 (av)	81.7(1)	98.3(1)			[37]
23	$[\mathrm{Me_2GaNCy_2}]_2$	Ga_2N_2 ring, planar	2.068 (av)	90.5(2)	89.5(2)	2.911(2)		[23]
25	$[\mathrm{Et_2GaNCy_2}]_2$	Ga_2N_2 ring, folded	2.069(5) (av)	87.2	87.9	2.875		[23]
63	$[\mathrm{Me_2GaNPh_2}]_2$	Ga_2N_2 ring, folded	2.088(4)	88.2(2)	87.8(2)	2.9008(1)		[40b]
Monomeric								
12	$[\mathrm{Cl_2Ga(thf)N(H)SiMe_3}]$	$X_2(L)GaN$ core, distorted tetrahedral	2.026(3)					[18]
47	$[\mathrm{Et_2GaN(^tBu)BMes_2}]$	R_2GaN core, planar	1.937(3)				69.7	[32]
27	$[\mathrm{^tBu_2GaN(1\text{-}Ad)SiPh_3}]$	R_2GaN core, planar	1.924(2)				71.8	[24]
5	$[\mathrm{H_2GaN(SiMe_3)_2(quin)}]$	$R_2(L)GaN$ core, distorted tetrahedral	1.913(2)					[11]

Table 1 (*Continued*)

No.	Compound	Framework	Bond length (Å)	Bond angles (°)		Bond length (Å)	Torsion angle (°) †	References
			M–N(amido)	N–M–N	M–N–M	M···M (Å)		
26	$[{}^t\text{Bu}_2\text{GaN}({}^t\text{Bu})\text{SiPh}_3]$	R_2GaN core, planar	1.906(5)				88.7	[24]
44	$[(\text{Trip})_2\text{GaNPh}_2]$	R_2GaN core, planar	1.878(7)				0	[24]
45	$[\text{Mes}^*_2\text{GaN(H)Ph}]$	R_2GaN core, planar	1.874(4)				6.7	[31]
28	$[\text{Mes}^*(\text{Cl})\text{GaN}(\text{SiMe}_3)_2]$	R(X)GaN core, planar	1.867(10)				3.1	[25]
43	$[\text{Trip}_2\text{GaN(H)Dipp}]$	R_2GaN core, planar	1.847(12)				8.3	[24]
46	$[\text{Mes}^*(\text{Cl})\text{GaN(H)Ph}]$	R(X)GaN core, planar	1.835(10)				3.0	[31]
			1.829(9)				1.8	
Gallium diamides								
Dimeric								
198	$[\text{Cy}_2\text{Ga}(\mu\text{-3,5-Me}_2\text{Pz})\text{MgCl(thf)}_2]$	Ga–(N–N–)$_2$–Mg ring, planar	2.02 (av)	106.4(2)				[92]
199	$[{}^n\text{Bu}_2\text{Ga}\{\mu\text{-N(H)2,6-Me}_2\text{C}_6\text{H}_3\}_2\text{Li(OEt}_2)]$	Ga–N–Li–N core, planar	2.009 (av)	94.4(3)				[37]
187	$[\text{N}_3\{\text{Me}_2\text{N}\}\text{Ga}\{\mu\text{-NMe}_2\}]_2$	Ga_2N_2 core, planar	1.995(2)^{br}	87.52(11)	92.48(11)	2.881(3)		[85]
			1.834(3)					
197	$[\text{Cy}_2\text{Ga}\{\mu\text{-N(H)}{}^t\text{Bu}\}\text{Li(thf)}_2]$	Ga–N–Li–N core, planar	1.99(2)	89.1(5)	86.3(8)			[92]
191	$\text{Cl}\overline{\text{GaN(SiMe}_3)\text{CH}_2\text{C(Me}_2)\text{CH}_2\text{N}}\text{SiMe}_3$	Ga_2N_2 core, slightly folded	1.994 ‡	92.1	87.1			[89]
			2.056					
189	$\text{Br}_2\overline{\text{GaN(SiMe}_3)\text{CH}_2\text{C(Me}_2)\text{CH}_2\text{N}}\text{-(H)SiMe}_3$	C_3GaN_2 ring, twisted	1.84	99.9(5)				[89]
			2.04					
Monomeric								
181	$[\text{HGa}\{\text{N(SiMe}_3)_2\}_2(\text{quin})]$	R(L)GaN_2 core, distorted tetrahedral	1.9315(13)	119.41(6)				[11]
			1.9138(13)					
176	$[(\text{tmp})_2\text{GaSi(SiMe}_3)_3]$	$RGaN_2$ core, planar	1.913(2)	121.8(1)			64.3	[83]
			1.908(3)				79.2	

Table 1 (*Continued*)

No.	Compound	Framework	Bond length (Å)	Bond angles (°)		Bond length (Å)	Torsion angle (°) †	References
			M–N(amido)	N–M–N	M–N–M	M···M (Å)		
177	$[(tmp)_2GaP(^tBu)_2]$	$PGaN_2$ core, planar	1.908(6) (av)	121.8(3)				[84]
182	$[HGa\{N(H)Dipp)_2\}(quin)]$	$R(L)GaN_2$ core, distorted tetrahedral	1.902(3) 1.899(2)	109.89(7)				[11]
179	$[Ga_2(tmp)_4]$	N_2Ga-GaN_2 core	1.901(4)	118.6 (av)		2.525(1)	53	[86]
185	$[\{Dipp(Me_3Si)N\}Ga(Cl)\{NDipp(SiMe_2)\ N(SiMe_3)Dipp\}]$	$XGaN_2$ core	1.858(3) 1.845(3)	137.2(2)				[28]
173	$[(tmp)_2GaPh]$	$RGaN_2$ core, planar	1.883(2)	129.0(1)				[30]
174	$[(tmp)_2GaOPh]$	$RGaN_2$ core, planar	1.849(3) 1.818(3)	133.9(1)				[30]
184	$[ClGa\{N(SiMe_3)_2\}_2]$	$XGaN_2$ core, planar	1.844(4) 1.834(4)	128.5(2)			49.5 40.5	[31]
183	$[Mes^*Ga\{N(H)Ph\}_2]$	$RGaN_2$ core, planar	1.837(8)	105.3(4)			7.3	[31]
Gallium triamides								
Dimeric								
209	$[\{Me_2N\}_2Ga\{\mu\text{-}NMe_2\}]_2$	Ga_2N_2 core, planar	$2.013(3)^{br}$ $1.855(4)^{t}$	87.7(1)	92.3(1)	92.3(1)	2.902	[98]
208	$[\{^tBu(H)N\}_2Ga\{\mu\text{-}N(H)^tBu\}]_2$	Ga_2N_2 core, non-planar	$2.008(8)^{br}$ $1.813(10)^{t}$	81.6(3)	94.8(4)			[97]
Monomeric								
216	$[Ga\{N(H)Dipp\}_3(py)]$	$LGaN_3$ core, distorted tetrahedral	1.871(8)	115.3				[101]
214	$[Ga\{N(SiMe_3)_2\}_3]$	GaN_3 core, planar	1.870(6) 1.868(1)	120.0			50 48.6	[97,102] [17,31]

Table 1 (*Continued*)

No.	Compound	Framework	Bond length (Å)	Bond angles (°)		Bond length (Å)	Torsion angle (°) †	References
			M–N(amido)	N–M–N	M–N–M	M···M (Å)		
Indium monoamides								
Polymeric								
154	[Me$_2$In(NC$_4$Me$_4$)]	R$_2$InN core, planar	2.197(3)			4.255		[76]
152	[Et$_2$In(Pyrr)]	R$_2$InN core, almost planar	2.166(4)				16.1	[68]
Dimeric								
132	[Me$_2$InN(SiMe$_3$)$_2$]$_2$	In$_2$N$_2$ ring, planar	2.305(5) (av)	89.7(1)	90.3(1)	3.270(1)		[66]
124	[Me$_2$InN(Me)Ph]$_2$	In$_2$N$_2$ ring, planar	2.282	85.08(7)	94.92(7)	3.363		[47]
167	[(^{t}Bu)$_2$InNEt$_2$]$_2$	In$_2$N$_2$ ring, folded	2.269 (av)	83.6(1)	96.2(2)	3.381(0)		[81]
168	[(^{t}Bu)$_2$InN(^{n}Bu)$_2$]$_2$	In$_2$N$_2$ ring, folded	2.268(4) (av)	84.1(1)	95.7(1)	3.367(1)		[81]
131	[Me$_2$InN(^{i}Pr)$_2$]$_2$	In$_2$N$_2$ ring, planar	2.263(6) (av)	87.8 (av)	90.4(2)	3.224(1)		[66]
133	[Me$_2$InN(GeMe$_3$)$_2$]$_2$	In$_2$N$_2$ ring, planar	2.260 (av)	88.1(1)	92.0 (av)	3.250(1)		[67]
166	[Me$_2$InN(^{i}Pr)SnMe$_3$]$_2$	In$_2$N$_2$ ring, planar	2.246(2) (av)	87.36(8)	92.64(8)	3.102(4)		[22]
130	[Me$_2$InNEt$_2$]$_2$	In$_2$N$_2$ ring, planar	2.235(3) (av)	86.0(2)	94.0(2)	3.269(1)		[66]
136	[(^{i}Pr)$_2$InN(H)^{t}Bu]$_2$	In$_2$N$_2$ ring, planar	2.234(4)	83.1(1)	96.9(1)	3.342(1)		[69]
122	[Me$_2$InN(CH$_2$)$_2$N(Me)CH$_2$CH$_2$]$_2$	In$_2$N$_2$ ring, planar	2.233 (av)	84.7(3)	95.3(2)			[62]
165	[Me$_2$InN(Me)SnMe$_3$]$_2$	In$_2$N$_2$ ring, planar	2.225(6) (av)	86.3(2)	93.7(2)	3.2454(9)		[22]
120	[Me$_2$InNMe$_2$]$_2$	In$_2$N$_2$ ring, planar	2.22(2)	85.7(4)	94.3(3)	3.278(2)		[61]
142	[^{i}Pr$_2$In{μ-N(H)^{t}Bu}$_2$In(Cl)^{i}Pr]	In$_2$N$_2$ ring, planar	2.214(1) (av)	83.9 (av)	96.1(6)	3.318(1)		[69]
164	[Et(Cl)InN(SnMe$_3$)$_2$]$_2$	In$_2$N$_2$ ring, planar	2.196(4) (av)	89.9(2)	90.1(2)			[80]
163	[Me(Cl)InN(SnMe$_3$)$_2$]$_2$	In$_2$N$_2$ ring, planar	2.193(4) (av)	89.81(4)	90.19(14)			[80]
141	[^{i}Pr(Cl)InN(H)^{t}Bu]$_2$	In$_2$N$_2$ ring, planar	2.185 (av)	83.4(2)	96.6(2)	3.163(1)		[69]
140	[MesIn(μ-Cl)N(SiMe$_3$)$_2$]$_2$	In$_2$Cl$_2$ ring, planar	2.020(9) (av)			3.872(2)		[69]
Monomeric								
146	[^{t}Bu$_2$InN(Dipp)SiPh$_3$]	R$_2$InN core, planar	2.104(3)				15.5	[71]
161	[Li(thf)$_3$][Cl$_3$InN(Dipp)SiMe$_3$]	Cl$_3$InN core, distorted tetrahedral	2.054(2)					[79]

Table 1 (*Continued*)

No.	Compound	Framework	Bond length (Å)	Bond angles (°)		Bond length (Å)	Torsion angle (°) †	References
			M–N(amido)	N–M–N	M–N–M	M···M (Å)		
Indium diamides								
203	[MeInN(Me)C_5H_4N]	$RInN_4$ core, square-pyramidal	2.14	113.0(2)				[62]
201	[Mes*In{N($SiMe_3$)$_2$}$_2$]	$RInN_2$ core, planar	2.103(6) 2.094(4)	119.4(2)			44.4 47.2	[25]
Indium triamides								
233	[Cs(FIn{N($SiMe_3$)$_2$}$_3$]	XnN_3 core, distorted tetrahedral	2.125 (av)	117.2(1) (av)				[106]
231	[In{N(H)Dipp}$_3$(py)$_2$]	L_2InN_3 core, distorted tbp	2.116(4)	116.6 (av)				[101]
226	[In{N(^{t}Bu)SiHMe$_2$}$_3$(*p*-Me$_2$Npy)]	$LInN_3$ core, distorted tetrahedral	2.125(3) (av)	116.0 (av)				[104]
225	[In{N(Ph)SiMe$_3$}$_3$OEt$_2$]	$LInN_3$ core, distorted tetrahedral	2.095(2) (av)	118.2 (av)				[104]
228	[In{NPh$_2$}$_3$(py)]	$LInN_3$ core, distorted tetrahedral	2.083(3) (av)	124.4 (av)				[104]
220	[In(tmp)$_3$]	InN_3 core, planar	2.078(5) (av)	120.0 (av)				[93]
221	[In{N(H)Mes*}$_3$]	InN_3 core, planar	2.068(7) (av)	120.0(1) (av)				[101]
227	[Li(thf)$_4$][In(NPh$_2$)$_3$Cl]	$XInN_3$ core, distorted tetrahedral	2.06 (av)	112.5 (av)				[104]
219	[In{N($SiMe_3$)$_2$}$_3$]	InN_3 core, planar	2.049(1)	120			48.6	[102]

† Angle between the perpendiculars to the MC_2 and NC_2 coordination planes unless otherwise indicated.

‡ Angles associated with the central Ga_2N_2 ring; ^{br}bridging; ^{t}terminal.

$$R_2MX + LiN(R')R'' \rightarrow [R_2MN(R')R'']_n + LiX \tag{1}$$

$$RMX_2 + LiN(R')R'' \rightarrow [R(X)MN(R')R'']_n + LiX \tag{2}$$

An alternative route to monoamido complexes involves the reaction of trivalent gallium or indium organometallics $[R_3M]$ with amines at elevated temperatures, according to Eq. (3).

$$R_2M + R'_2NH \rightarrow [R_2MNR'_2]_n + RH \tag{3}$$

Further synthetic approaches that were utilised to prepare some of the early monoamides of gallium are based on silyl- or stannyl-halide elimination from the reaction of either a metal halide or an organometallic halide complex with a silyl- or stannyl-amine e.g. Eqs. (4) and (5). In addition, monoamidogallane complexes can be prepared via the reaction of gallane with amines Eq. (6).

$$RMX_2 + (Me_3Si)_2NH \rightarrow [R(X)MN(H)SiMe_3]_n + Me_3SiX \tag{4}$$

$$MX_3 + (Me_3Si)_2NR' \rightarrow [X_2MN(R')SiMe_3]_n + Me_3SiX \tag{5}$$

$$\underset{\text{e.g. L = NMe}_3}{[GaH_3(L)]} + HNR'_2 \rightarrow \underset{n\,=\,2\text{ or }3}{1/n[H_2GaNR'_2]_n} + H_2 + L \tag{6}$$

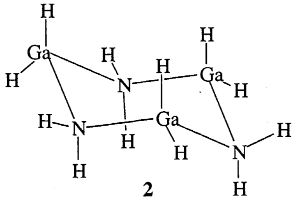
Monoamides, of type $[R_2MNR'_2]_n$ (R = halide, akyl or aryl; M = Ga or In; R′ = alkyl, aryl or silyl), have been structurally characterised for both gallium and indium, as discussed in detail below. Many monoamido complexes are dimeric or trimeric and the ring size and conformation of these compounds is dependent on substituent steric requirements as well as entropy factors and ring strain.

2.1. Gallium

More than 30 years ago, it was reported that the reaction of amines with $[GaH_3(NMe_3)]$ affords complexes of type $[H_2GaNR_2]_n$ [Eq. (6)] [5]. The crystal structure of $[H_2Ga\overline{NCH_2CH_2}]_3$ (**1**) was investigated by X-ray diffraction and showed a $(GaN)_3$ ring in the chair conformation, with a Ga–N bond distance of 1.97(9) Å [6]. The average N–Ga–N and Ga–N–Ga angles in **1** are 100 and 116°, respectively. Treatment of $[GaH_3(NMe_3)]$ with NH_3 (gas or liquid phase) resulted in the isolation of cyclotrigallazane, $[H_2GaNH_2]_3$ (**2**) [7,8]. Interestingly, it is also possible to prepare compound **2** via the reaction between $LiGaH_4$ and NH_4X (X = Cl, Br), according to Eq. (7) [9].

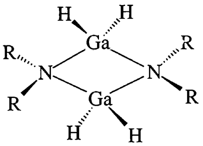
$$\underset{\text{X = Cl, Br}}{3LiGaH_4} + 3NH_4X \rightarrow [H_2GaNH_2]_3 + 6H_2 + 3LiX \tag{7}$$

The structure of **2** was shown to be similar to that of **1** with the six-membered $(GaN)_3$ ring adopting a chair conformation. The average Ga–N bond distance is 1.981(4) Å and the average N–Ga–N and Ga–N–Ga angles are 100.3(5) and 117.1(3)°, respectively [8]. In the solid state, individual molecules of **2** are connected by unusual Ga–H···H–N hydrogen bonds.



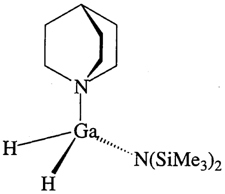
2

Pyrolysis of **2** was shown to result in rare cubic/hexagonal layers of gallium nitride (GaN) [8]. In contrast to **2**, the solid-state structures of $[H_2GaNR_2]_2$ (**3**, R = Me; **4**, R = Et) comprise dimeric molecules [5,10]. The gallium and nitrogen atoms adopt distorted tetrahedral geometries in both structures and the central planar Ga_2N_2 ring is almost square (**3**, avg. Ga–N 2.027(4) Å; **4**, avg. Ga–N 2.017 Å).



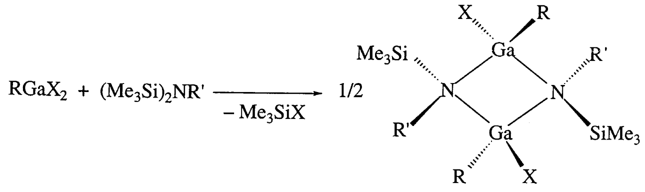
3, R = Me; **4**, R = Et

Until recently, there were no examples of monomeric complexes of monoamidogallanes. The first example of such a complex (**5**) was isolated from the reaction between $[Ga(Cl)H_2(quin)]$ and 1 equiv. of $LiN(SiMe_3)_2$ [11]. An X-ray diffraction study confirmed the monomeric nature of **5** and revealed that the tetracoordinate gallium centre adopts a distorted tetrahedral geometry. The Ga–N(amido) bond distance in **5** is shorter than those observed in **1**–**4** (Ga–N 1.913(2) Å) [11]. The geometry at the amido nitrogen atom is almost planar with the sum of the angles at the nitrogen being 358.6°. Attempts to synthesise the ligand free complex, $[H_2GaN(SiMe_3)_2]_n$ from the reaction of $[GaH_3(NMe_3)]$ and $N(SiMe_3)_3$ were unsuccessful [12].



5

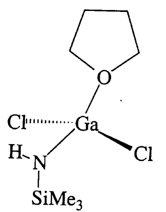
As mentioned above, one of the synthetic approaches to monoamido gallium complexes involves dehalosilylation reactions Eqs. (4) and (5). Thus, the reaction between hexamethyldisilazane [HMDS, $(Me_3Si)_2NH$] and either $[MeGaCl_2]$ or $[^nBuGaCl_2]$ has been reported to yield the monoamides $[Me(Cl)GaN(H)SiMe_3]_2$ (**6**) and $[^nBu(Cl)GaN(H)SiMe_3]_2$ (**7**), respectively [13]. An X-ray analysis of **6** demonstrated that this compound exists as an amido-bridged dimer in the solid state. The substituents on the four-membered Ga_2N_2 ring adopt a *trans–trans* conformation in which the alkyl groups are *trans* to each other and the trimethylsilyl groups are *trans* to each other. The Ga_2N_2 ring in **6** is almost planar with internal ring angles of 89.0° at gallium and 91.2(2)°. The Ga–N bond distances of 2.012(8) Å in **6** are similar to those observed in **3** and **4**. Recently, the reaction between HMDS and $MeGaBr_2$ was reported to yield the analogous complex $[Me(Br)GaN(H)SiMe_3]_2$ (**8**) [14].



6: R = Me, X = Cl, R' = H
7: R = ⁿBu, X = Cl, R' = H
8: R = Me, X = Br, R' = H
9: R = X = Cl, R' = H
10: R = X = Br, R' = H
13: R = X = Cl, R' = Me

When the reactions between HMDS and 1 equiv. of GaX_3 (X = Cl or Br) were carried out, the dimeric products $[Cl_2GaN(H)SiMe_3]_2$ (**9**) and $[Br_2GaN(H)SiMe_3]_2$ (**10**) were formed [15,16]. The crystal structures of both compounds were determined and are very similar to that of **6** with planar Ga_2N_2 rings. In both compounds the *trans* isomer of each dimer was isolated and the Ga–N bond distances were found to be shorter than those observed in **6** (**9**, Ga–N 1.969(4) Å; **10**, Ga–N 1.996(16) Å). The internal ring angles in **9** and **10** are similar to those observed in **6**. Therefore, the replacement of chlorine atoms in **9** with bromine atoms has little effect on the structural features of the *trans* dimer. The NMR data indicated that in solutions of **9** equilibrium mixtures of $[Cl_2GaN(H)SiMe_3]_3$, *trans*-$[Cl_2GaN(H)SiMe_3]_2$ and *cis*-$[Cl_2GaN(H)SiMe_3]_2$ were present. In contrast, a trimer–dimer equilibrium is absent in solutions of **10**, which is probably due to the larger size of the bromine atoms preventing the formation of the trimer, $[Br_2GaN(H)SiMe_3]_3$. However, a mixture of *trans*-$[Br_2GaN(H)SiMe_3]_2$ and *cis*-$[Br_2GaN(H)SiMe_3]_2$ are present in solutions of **10**. Interestingly, a tetrameric gallium imido complex, $[MeGaNSiMe_3]_4$ (**11**), with a cubic Ga_4N_4 core, has been isolated from the reaction of **10** with lithium methanide [17].

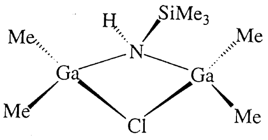
The structure of the tetrahydrofuran-coordinated monomer of compound **9**, $[Cl_2(thf)GaN(H)SiMe_3]_2$ (**12**), was reported recently [18]. The crystal structure of **12** revealed that the tetracoordinate gallium centre adopts a distorted tetrahedral geometry. The Ga–N bond distances in **12** are slightly longer than those found in **9** (Ga–N 2.026(3) Å).



12

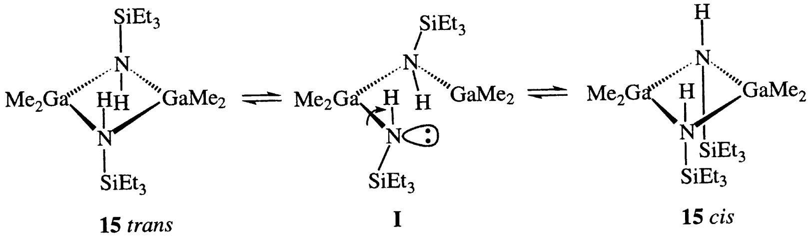
Treatment of $GaCl_3$ with $(Me_3Si)_2NMe$ resulted in the isolation of $[Cl_2GaN(Me)SiMe_3]_2$ (**13**) [15]. The structure of **13** was shown to be very similar to those of **6**, **9** and **10** by X-ray crystallography. Thus, the *trans* isomer is adopted with average Ga–N bond distances of 1.986(5) Å and angles at the gallium and nitrogen atoms of 90°. Interestingly, in solutions of **13** only the *cis* and *trans* dimers were identified (no trimers were present). The related phosphoraneiminato complexes, $[X_2Ga(NPPh_3)]_2$ ($X = Cl$ or I) and $[I_2Ga(NPEt_3)]_2$, were prepared in a similar manner from the reaction of GaX_3 with $R_3PNSiMe_3$ [19].

The reaction between a dialkylgallium halide, $[Me_2GaCl]$ and HMDS resulted in the formation of the cyclic (1:1) adduct $[\{Me_2GaN(H)SiMe_3\} \cdot Me_2GaCl]$ (**14**) [14]. The solid-state structure of **14** comprises dimeric molecules in which the $N(H)SiMe_3$ and Cl groups act as bridging ligands resulting in a folded $\overline{\text{Ga–N–Ga–Cl}}$ ring. The Ga–N distance of 2.000(3) Å is slightly longer than those observed in **9** and **10**. The N–Ga–Cl, Ga–N–Ga and Ga–Cl–Ga angles in **14** are 87.12(11), 102.2(2) and 79.79(5)°, respectively.



14

Gallium silylamido complexes can also be prepared from the reaction of Et_3SiNH_2 with $[R_3Ga]$ ($R = Me$, Et) [20]. A mixture of *trans* and *cis* isomers of $[R_2GaN(H)SiEt_3]_2$ (**15**, $R = Me$, *trans*:*cis* 1.5:1; **16**, $R = Et$, *trans*:*cis* 1.3:1) were isolated. Purification of **15** by sublimation or recrystallisation afforded colourless



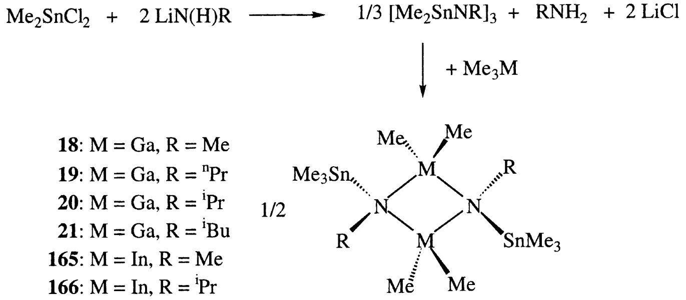
Scheme 1.

crystals of *trans*-$[Me_2GaN(H)SiEt_3]_2$, but in solution it equilibrated with the *cis* isomer. The *trans* → *cis* isomerisation of **15** has been studied by ^{1}H-NMR spectroscopy. The proposed isomerisation pathway involves the initial breaking of a Ga–N bond to form species **I**, followed by rotation about the non-bridged Ga–N bond and rebridging, as shown in Scheme 1.

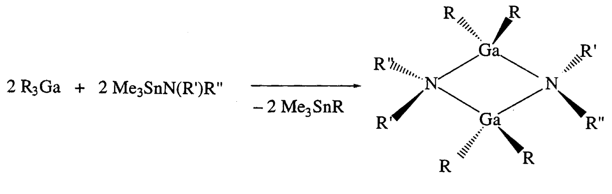
The crystal structure of **15** showed that this compound exists as an amide-bridged dimer. The Ga_2N_2 unit is planar (avg. N–Ga–N 88.2(2)°) and the Ga–N bond distances of 2.025(4) and 2.033(4) Å are slightly longer than those observed in the dimeric silylamido complexes described above (**6**, **9**, **10** and **13**). The related reaction between $[Me_3Ga]$ and 1,1,3,3-tetramethyldisilazane resulted in the formation of dimeric $[Me_2GaN(SiHMe_2)_2]_2$ (**17**) [21]. As expected, the structure of **17** is similar to **15** and comprises a planar Ga_2N_2 four-membered ring.

A novel route for the generation of stannylamido gallium complexes has been reported [22]. As summarised in Scheme 2, the initial step involves the reaction of $[Me_2SnCl_2]$ with 2 equiv. of LiN(H)R to form the trimeric species $[Me_2SnNR]_3$. The final step involves the reaction of the trimer $[Me_2SnNR]_3$ with $[Me_3Ga]$ to form the desired monoamido complexes $[Me_2GaN(R)SnMe_3]_2$ (**18**, R = Me; **19**, R = ^{n}Pr; **20**, R = ^{i}Pr; **21**, R = ^{t}Bu) along with other products. The structures of **19** and **20** are similar in that they comprise dimeric molecules in which the $N(R)SnMe_3$ groups act as bridging ligands. The central Ga_2N_2 ring in both **19** and **20** is planar with similar internal ring angles. As expected, the Ga–N bond distances in both complexes are similar to those found in **14** and **16** (**19**, avg. Ga–N 2.022(5) Å; **20**, avg. Ga–N 2.070(3) Å).

The synthesis of a range of substituted aminogallanes via alkyltrimethyltin elimination has also been reported [23]. The reaction of $[R_3Ga]$ with $[Me_3SnN(R')R'']$ resulted in the formation of the 1:1 complexes $[R_2GaN(R')R'']_2$ (**20** and **22**–**25**). The structures of **23**–**25** indicate that they are all dimeric in the solid state. The Ga_2N_2 rings are non-planar in **24** and **25** with fold angles on the Ga···Ga diagonals of 148.7(3) and 146.3(3)° (**24**, N–Ga–N 87.2°, Ga–N–Ga 87.9°; **25**, N–Ga–N 87.4°, Ga–N–Ga 88.4°). In contrast, compound **23** possesses a planar Ga_2N_2 ring with internal ring angles of 90.5(2)° at gallium and 89.5(2)° at nitrogen. The Ga–N bond distances are all similar and range 2.039(4) to 2.070(5) Å.

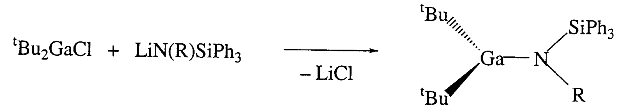


Scheme 2.

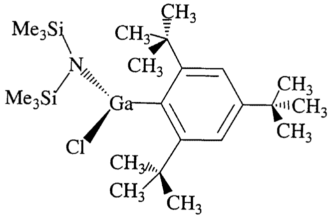


20: R = Me, R' = ^{i}Pr, R'' = $SnMe_3$
22: R = Me, R' = R'' = ^{i}Bu
23: R = Me, R' = R'' = Cy
24: R = Et, R' = R'' = ^{i}Bu
25: R = Et, R' = R'' = Cy

A series of monomeric complexes incorporating silylamido ligands have also been reported [24,25]. Thus, the reaction of [^{t}Bu$_2$GaCl] with 1 equiv. of $LiN(R)SiPh_3$ (R = ^{t}Bu or 1-Ad) resulted in the formation of the monoamides [^{t}Bu$_2$GaN(R)SiPh$_3$] (**26**, R = ^{t}Bu; **27**, R = 1-Ad) [24]. The reaction between [Mes*$GaCl_2$] and 1 equiv. of $LiN(SiMe_3)_2$ afforded the monomeric complex [Mes*(Cl)GaN$(SiMe_3)_2$] (**28**) [25]. The monomeric nature of **26**–**28** was confirmed by X-ray diffraction and revealed that the gallium and nitrogen centres in all the complexes have essentially planar coordination. The gallium and nitrogen planes are twisted relative to each other (88.7° in **26** and 71.8° in **27**). Similarly, in **28** the plane of the Mes* ring is orientated almost perpendicular (86.9°) to the coordination plane at gallium so as to minimise steric repulsion between the two bulky ligands. This results in a weak interaction between the hydrogen atoms from the *o*-^{t}Bu groups to the gallium centre (avg. Ga···H 2.316 Å). The Ga–N bond distances in **26** (1.906(5) Å) and **27** (1.924(2) Å) are slightly longer than that in **28** (1.867 Å).



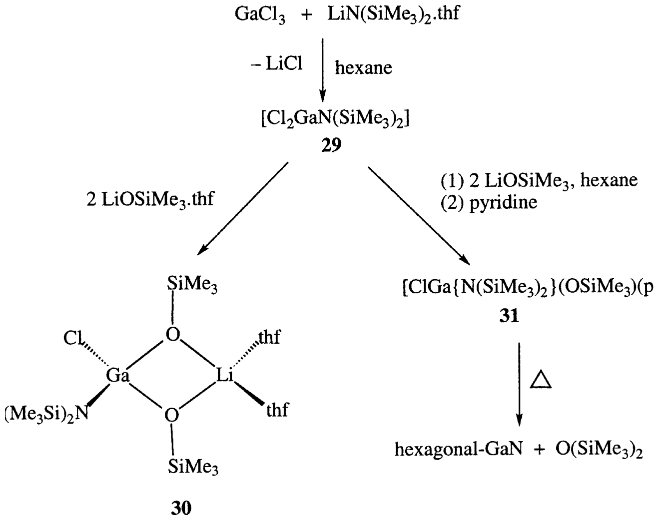
26: R = ^{t}Bu
27: R = 1-Ad



28

It is worth noting at this point that metal–nitrogen bond lengths up to 0.2 Å shorter than the sum of covalent radii may be observed in gallium and indium amides [2a,2b]. A number of factors can influence the bond distances that are observed. For example, differences in electronegativity between M and N can lead to bond shortening through an ionic contribution to the bond strength. However, empirical corrections of the bond distances for ionic effects results in values close to those observed experimentally [2a]. As discussed in the introduction, efficient π-overlap requires a coordination number of 3 (or less) and a planar geometry at both atoms along with the alignment of their coordination planes. In compounds **26** and **27**, large torsion angles are observed and so the requisite geometry for π-overlap is not achieved. If the correct geometry for overlap is achieved, it will be weak and so small rotation barriers around these bonds are expected. Therefore, a bond length that is shorter than the sum of the covalent radii of M and N, does not necessarily imply the presence of π-bonding.

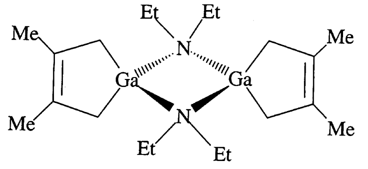
The reaction between $GaCl_3$ and $LiN(SiMe_3)_2$ resulted in the preparation of the silylamido complex $[Cl_2GaN(SiMe_3)_2]$ (**29**), according to Scheme 3 [26]. Unfortunately, no information regarding the structure of **29** is available; however, the reactivity of **29** has been investigated. Thus, the reaction of **29** with $LiOSiMe_3 \cdot thf$ results in the formation of one of two products depending on the presence of coordinating solvents. When the aforementioned reaction is carried out in thf, the ionic complex $[Li(thf)_2][ClGa\{N(SiMe_3)_2\}(OSiMe_3)_2]$ (**30**) is formed. The crystal structure of **30** was investigated by X-ray diffraction and showed a pseudotetrahedral geometry at gallium with a Ga–N distance of 1.883(10) Å. The siloxide oxygen atoms bridge the anion and the cation. In contrast, when the reaction between **29** and $LiOSiMe_3 \cdot thf$ is carried out in the presence of pyridine, the neutral complex $[ClGa\{N(SiMe_3)_2\}(OSiMe_3)(py)]$ (**31**, py = pyridine) is produced. No structural data are available for compound **31**; however, hexagonal GaN is produced when **31** is heated to 210 °C and annealed at 350 °C for 8 h. A related (alkoxy)gallium amide, $[Cl(tmp)Ga(\mu\text{-}OEt)]_2$ (**32**) has also been reported [27]. The solid-state structure of **32** comprises dimeric molecules in which the OEt groups act as



Scheme 3.

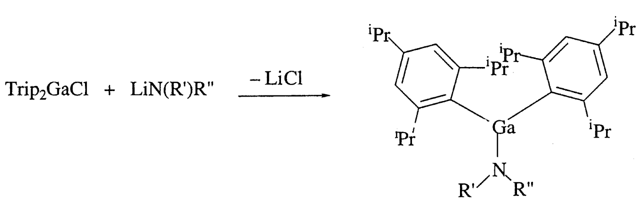
bridging ligands. In addition, oxidation of $[Et_2Ga\{N(SiMe_3)Dipp\}]_2$ (**33**) resulted in the formation of the (alkoxy)gallium amide $[EtGa\{N(SiMe_3)Dipp\}(\mu\text{-}OEt)]_2$ (**34**) [28].

The dichloro(dialkylamido)gallium complexes, $[Cl_2GaNEt_2]_2$ (**35**) and $[Cl_2Ga(pip)]_2$ (**36**), have been synthesised from the reaction of $GaCl_3$ with the appropriate lithium dialkylamides [29]. No structural data are available for compounds **35** and **36**. However, the reaction of **35** or **36** with $Mg(C_4H_6)(thf)_2$ produces mixtures of dimeric and trimeric $[(C_4H_6)Ga(NR_2)]_n$ ($n = 2$ or 3; **37**, R = Et; **38**, NR_2 = pip), whereas the reaction with $Mg(2,3\text{-}Me_2C_4H_4)(thf)_2$ results in the formation of dimeric $[(2,3\text{-}Me_2C_4H_4)GaNR_2]_2$ (**39**, R = Et; **40**, NR_2 = pip) [29]. The structure of **39** consists of a slightly non-planar Ga_2N_2 core with an average Ga–N bond distance of 2.007 Å. The internal ring angles at gallium and nitrogen are 87.6 and 92.1°, respectively.

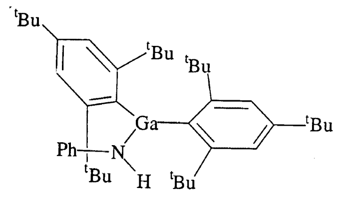


39

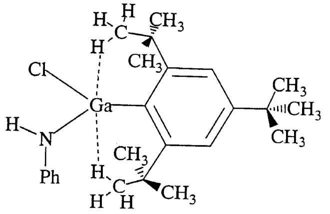
Salt elimination routes [Eq. (1)] were also used for the preparation of a series of monomeric monoamidogallanes of type $[R_2GaN(R')R'']$ (**41**, R = Me, $N(R')R''$ = tmp [30]; **42**, R = Et, $N(R')R''$ = tmp [30]; **43**, R = Trip, $R' = H$, R'' = Dipp [24]; **44**, R = Trip, $R' = R''$ = Ph [24]; **45**, R = Mes*, $R' = H$, R'' = Ph [31]). In addition, the reaction between $[Mes^*GaCl_2]$ and $[(thf)MgNPh]_6$ resulted in the isolation of the monomeric complex $[Mes^*(Cl)GaN(H)Ph]$ (**46**) [31]. The structures of **43**–**46** were determined and revealed that the gallium centre in all the complexes is coordinated in an almost trigonal planar fashion. The coordination at nitrogen is also planar and the Ga–N bond lengths in **43**–**46** fall within the predicted single bond ranges and there is no clear evidence for Ga–N π-bonding in these species. In contrast to **26** and **27**, compounds **43**–**46** have short Ga–N bond lengths and low torsion angles (< 10°) suggesting that steric rather than π-bonding effects are determining the geometry and affecting the bond lengths. In compound **46**, the plane of the Mes* ring is almost perpendicular to the coordination plane at gallium and, in a manner similar to **28**, the *o*-^{t}Bu groups are located such that there are extremely short interactions between the C–H hydrogens and gallium (avg. Ga···H 2.04 Å).



43: R' = H, R" = Dipp
44: R' = R" = Ph

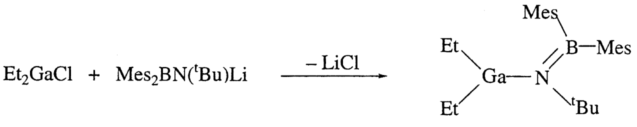


45



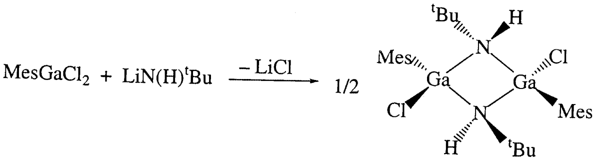
46

The reaction between $Mes_2BN(^tBu)Li$ and $[Et_2GaCl]$ resulted in the formation of $[Et_2GaN(^tBu)BMes_2]$ (**47**). Interestingly, compound **47** has a longer Ga–N bond length than observed in **43**–**46** (Ga–N 1.937(3) Å) [32]. This gives partial evidence for the existence of some π-interaction in the Ga–N bond, which in this case is weakened by a competitive B–N π-interaction [2]. However, some of the electron density on nitrogen may be delocalised onto boron resulting in a reduced Ga–N ionic interaction. In the structure of **47**, the coordination at gallium, nitrogen and boron is essentially planar with a torsion angle of 69.7° between the gallium and nitrogen planes.



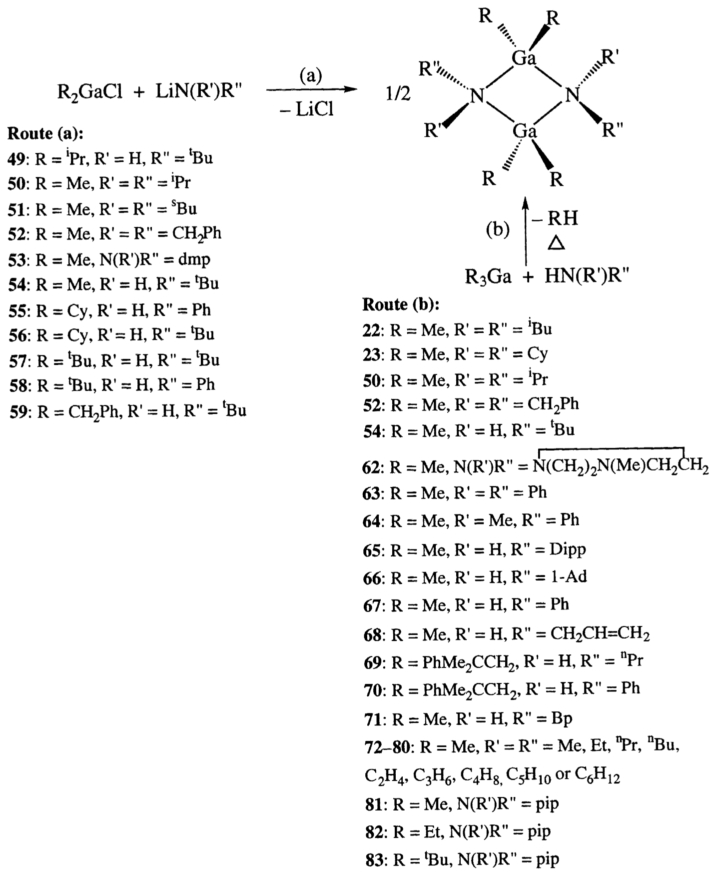
47

When less bulky substituents are present at the gallium centre, dimeric structures with four coordinate Ga and N centres are produced (similar to compounds **3**, **4**, **6**–**10**, **13** and **15**–**25**). Such complexes can be prepared using salt elimination reactions or alkane elimination [Eqs. (1)–(3)]. Thus, the reaction of $[MesGaCl_2]$ with $LiN(H)^tBu$ resulted in the formation of $[Mes(Cl)GaN(H)^tBu]_2$ (**48**) [33].



48

Dimeric monoamido complexes, of type $[R_2GaN(R')R'']_2$, have also been isolated from the reaction of $[R_2GaCl]$ with $LiN(R')R''$, [R = ^{i}Pr, R′ = H, R″ = ^{t}Bu [33], R = Me, R′ = R″ = ^{i}Pr, ^{s}Bu, CH_2Ph [34], R = Me, R′ = H, R″ = ^{t}Bu [35a], R = Me, N(R′)R″ = dmp [36], R = Cy or ^{t}Bu, R′ = H, R″ = ^{t}Bu, Ph [35,37], R = CH_2Ph, R′ = H, R″ = ^{t}Bu [38], according to Scheme 4 (**49**–**59**) [33–39]. The structures of **48**, **49**, **52** and **54**–**59** were determined and revealed that all the complexes are nitrogen-bridged dimers with a planar Ga_2N_2 four-membered ring (with the excep-



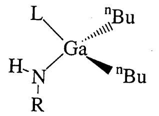
Route (a):
49: R = ^{i}Pr, R' = H, R" = ^{t}Bu
50: R = Me, R' = R" = ^{i}Pr
51: R = Me, R' = R" = ^{s}Bu
52: R = Me, R' = R" = CH_2Ph
53: R = Me, N(R')R" = dmp
54: R = Me, R' = H, R" = ^{t}Bu
55: R = Cy, R' = H, R" = Ph
56: R = Cy, R' = H, R" = ^{t}Bu
57: R = ^{t}Bu, R' = H, R" = ^{t}Bu
58: R = ^{t}Bu, R' = H, R" = Ph
59: R = CH_2Ph, R' = H, R" = ^{t}Bu

Route (b):
22: R = Me, R' = R" = ^{i}Bu
23: R = Me, R' = R" = Cy
50: R = Me, R' = R" = ^{i}Pr
52: R = Me, R' = R" = CH_2Ph
54: R = Me, R' = H, R" = ^{t}Bu
62: R = Me, N(R')R" = $\overline{N(CH_2)_2N(Me)CH_2CH_2}$
63: R = Me, R' = R" = Ph
64: R = Me, R' = Me, R" = Ph
65: R = Me, R' = H, R" = Dipp
66: R = Me, R' = H, R" = 1-Ad
67: R = Me, R' = H, R" = Ph
68: R = Me, R' = H, R" = $CH_2CH{=}CH_2$
69: R = $PhMe_2CCH_2$, R' = H, R" = ^{n}Pr
70: R = $PhMe_2CCH_2$, R' = H, R" = Ph
71: R = Me, R' = H, R" = Bp
72–80: R = Me, R' = R" = Me, Et, ^{n}Pr, ^{n}Bu, C_2H_4, C_3H_6, C_4H_8, C_5H_{10} or C_6H_{12}
81: R = Me, N(R')R" = pip
82: R = Et, N(R')R" = pip
83: R = ^{t}Bu, N(R')R" = pip

Scheme 4.

tion of **52** where the Ga_2N_2 ring is very slightly folded). The internal ring angles associated with the molecular core range from 81.7 to 85.0° at gallium and from 94.7 to 98.3° at nitrogen (see Table 1 and the discussion below). The Ga–N bond lengths are all similar and range between 2.001(7) and 2.069(3) Å; for compounds **48** and **54**–**59** the *trans* conformation is adopted.

A similar reaction between [^{n}Bu$_2$GaCl] and LiN(H)R, in the presence of a coordinating solvent (thf or pyridine), resulted in the isolation of the monomeric species [^{n}Bu$_2$Ga{N(H)R}(L)] (**60**, R = ^{t}Bu, L = thf; **61**, R = 2,6-$Me_2C_6H_3$, L = pyri-



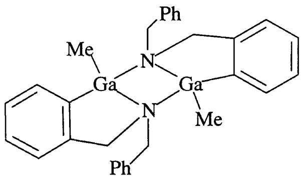
60: R = ^{t}Bu, L = thf
61: R = 2,6-$Me_2C_6H_3$, L = pyridine

dine) [37]. Unfortunately, no information regarding the structures of these complexes is available.

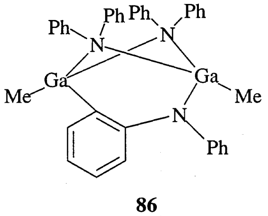
The reactions of trialkylgallium species [R_3Ga] with 1 equiv. of HN(R′)R″ (R = Me, R′ = H, R″ = Dipp, 1-Ad, Ph [40a,41], ^{t}Bu [42], $CH_2CH{=}CH_2$ [43] or Bp [45]; R = $PhMe_2CCH_2$, R′ = H, R″ = ^{n}Pr or Ph [44]; R = Me, N(R′)R″ = $\overline{N(CH_2)_2N(Me)CH_2C}H_2$; R = Me, R′ = R″ = Me, Et, ^{n}Pr, ^{i}Pr, ^{n}Bu, ^{i}Bu, Cy, Ph, CH_2Ph, C_2H_4, C_3H_6, C_4H_8, C_5H_{10} or C_6H_{12} [34a,34b,40b,45]; R = Me, Et or ^{t}Bu, N(R′)R″ = pip [46]; R = Me, R′ = Me, R″ = Ph [47]) at elevated temperatures resulted in the formation of the dimeric complexes **22**, **23**, **50**, **52**, **54** and **62**–**83**, as summarised in Scheme 4. The structures of **23**, **54**, **62**, **63** and **65**–**70** are similar to those observed for **48**, **49**, **52** and **54**–**59** and they are nitrogen bridged dimers with Ga–N bond distances ranging from 2.011(2) to 2.088(4) Å. The Ga_2N_2 core is planar in all the complexes with the exception of compounds **63**, **65** and **66** where it is folded slightly [40]. In compounds **54** and **65**–**70**, the bridging NHR groups take up a mutually *trans* arrangement which has been observed previously for all other known amidogallanes. However, compound **54** exists, in solution, as a mixture of *trans*- and *cis*-[$Me_2GaN(H)^tBu$]$_2$ as was observed for **15** and **16** [20,42]. The Ga–N bond distance in the related complex [$Me_2GaNCMe_2$]$_2$ (**84**) is shorter at 1.989(4) Å [48]. The internal angles in the planar Ga_2N_2 core in **84** are 82.1° at gallium and 97.9° at nitrogen.

For comparison, Table 1 contains selected X-ray structural data for a number of dimeric monoamido gallium complexes. The angles about the gallium and nitrogen atoms in all the compounds are highly distorted from tetrahedral which is typical for four-membered rings. The internal Ga–N–Ga and N–Ga–N angles are similar in all the compounds, with the Ga–N–Ga angles usually having slightly larger values than the N–Ga–N angles. Furthermore, these angles are generally significantly smaller than the external C–Ga–C and C–N–C angles. This is similar to the related aminoalanes, the structural data for which have been discussed recently [3]. As expected, the nature of the ligands on gallium and nitrogen influences the geometry of the central Ga_2N_2 ring. In general, these dimeric aminogallane complexes have planar Ga_2N_2 rings, except if a sterically demanding substituent is present, for example, in **65** and **66** where the ring is slightly folded.

Interestingly, heating compound **52** resulted in the isolation of the orthometallated species, [$Me\overline{GaN(CH_2C}_6H_4)(CH_2Ph)$]$_2$ (**85**) after recrystallisation [34b]. The solid-state structure of **85** comprises dimeric molecules with a planar Ga_2N_2 core (N–Ga–N 90.1(7)°; Ga–N–Ga 89.3(1)°). The Ga–N bond distance associated with the orthometallated rings is longer than the other set of Ga–N bond distances (2.045(3) vs. 2.018(3) Å). Similarly, when compound **63** was heated in toluene, the orthometallated species [$MeGaNPh_2$]$_2$($NPhC_6H_4$) (**86**) was formed [40b]. Compound **86** is composed of ($MeGaNPh_2$) units with a Ga_2N_2 folded core structure in which the two Ga centres are bridged by an *ortho*-deprotonated and bidentate $NPhC_6H_4$ ligand. Within the Ga_2N_2 ring, the Ga–N distances average 2.053(11) Å. The terminal Ga–N distance is 1.892(3) Å.



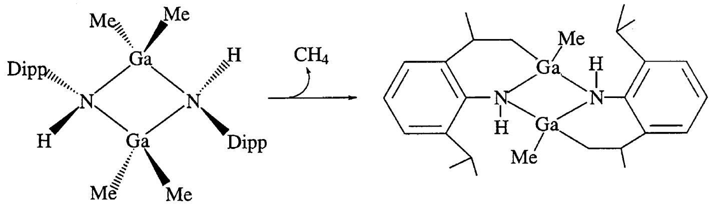
85



86

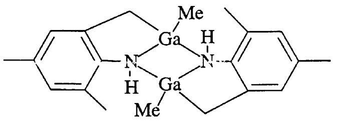
The related orthometallated species $[\mathrm{MeGa\{\mu\text{-}NHC_6H_3\text{-}^{i}Pr\text{-}6\text{-}CMeHCH_2\text{-}2\}}]_2$ (**87**) was formed when compound **65** was heated to 190 °C [40]. The structure of **87**, as expected, is very similar to that observed for **65** with the gallium coordinated to one methyl group and one of the *o*-^{i}Pr groups rather than to two methyl groups. The Ga_2N_2 core is planar (avg. N–Ga–N 86.4(2)°) and the average Ga–N distance is 2.025(4) Å.

Heating $\mathrm{MesNH_2}$ with $[\mathrm{Me_3Ga}]$ to 240 °C resulted in the direct isolation of the orthometallated compounds $[\mathrm{MeGa\{\mu\text{-}NHC_6H_2Me_2\text{-}4,6\text{-}CH_2\text{-}2\}}]_2$ (**88**) and $[\mathrm{Ga\{\mu\text{-}NHC_6H_2Me\text{-}4,6,13,15\text{-}CH_2\text{-}2,11\}_2GaMe_2}]$ (**89**) [40a]. The isomers **88** and **89** are similar to **87** since they are derived from metallation of the *ortho* substituent of the aromatic group. Moreover, both are presumed to be derived from similar precursors in which the –NHDipp group is replaced by an –NHMes group. Compound **88** comprises a dimeric $[\mathrm{MeGa\{\mu\text{-}NHC_6H_2Me_2\text{-}4,6\text{-}CH_2\text{-}2\}}]_2$ unit in which each gallium is coordinated to one methyl and one $-\mathrm{CH_2Ar}$ group rather than to two methyls as in the precursor.

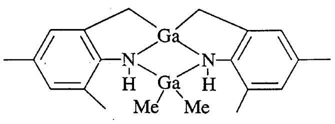


65 **87**

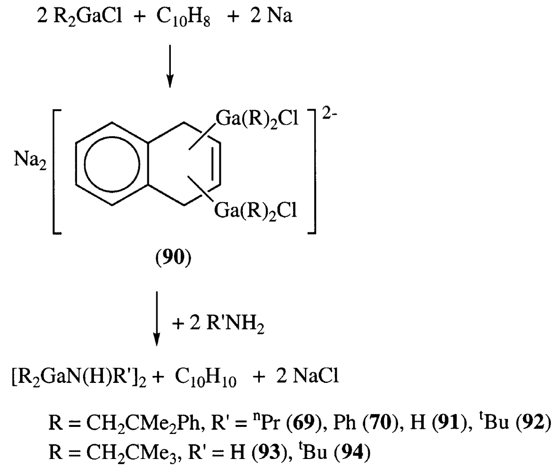
Compound **89** consists of a $[\mathrm{Ga\{\mu\text{-}NHC_6H_2Me\text{-}4,6,13,15\text{-}CH_2\text{-}2,11\}_2GaMe_2}]$ unit where one gallium is bonded to two $-\mathrm{CH_2Ar}$ groups and the other gallium remains bonded to two methyls. Therefore, each gallium is involved in bonding to one *o*-$\mathrm{CH_2}$ group in **88**, but only one gallium participates in such bonding in compound **89**. The Ga_2N_2 core in **88** is planar whereas in **89** there are minor deviations from planarity. The internal ring angles in the Ga_2N_2 unit in **88** and **89** are similar (**88**, N–Ga–N 87.7(2), Ga–N–Ga 92.3(4)°; **89**, N–Ga–N 87.9(4), Ga–N–Ga 92.0(4)°).



88

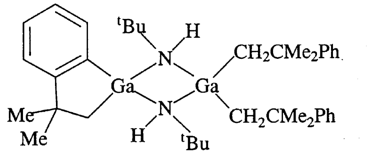


89

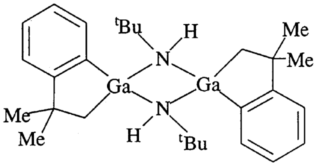


Scheme 5.

An alternative synthetic approach for the preparation of compounds **69** and **70** and some related amidogallanes has been reported, as summarised in Scheme 5 [44]. The first step involves the preparation of the dihydronapthalene derivative $[Na_2\{(C_{10}H_8)[Ga(R)_2Cl]_2\}]$ (**90**). Reacting **90** with $R'NH_2$ resulted in the formation of $[(R)_2GaN(H)R']_2$ (**69**; **70**; **91**, $R = PhMeCCH_2$, $R' = H$; **92**, $R = PhMeCCH_2$, $R' = {}^tBu$; **93**, $R = CH_2CMe_3$, $R' = H$; **94**, $R = CH_2CMe_3$, $R' = {}^tBu$) in high yield along with $C_{10}H_{10}$ and NaCl. The structure of compound **92** is similar to **69** and **70** in that the dimeric molecules consist of a planar Ga_2N_2 core (avg. Ga–N 2.050(3) Å; N–Ga–N 84.2(1)°; Ga–N–Ga 95.8(1)°). Interestingly, the reaction of $[Ga(CH_2CMe_2Ph)_3]$ with ${}^tBuNH_2$ results in the orthometallated complexes **95** and **96**. The structure of **95** has been determined and reveals a puckered or 'butterfly' conformation of the Ga_2N_2 core. The angle of distortion about the Ga···Ga axis is 21.9°. The Ga–N bond distances vary somewhat with those to the $Ga(CH_2CMe_2Ph)_2$ group being longer (avg. 2.046 Å). Compounds **95** and **96** differ from **87**–**89** since in the latter complexes the metallated aromatic ring was bonded to nitrogen and not to gallium.

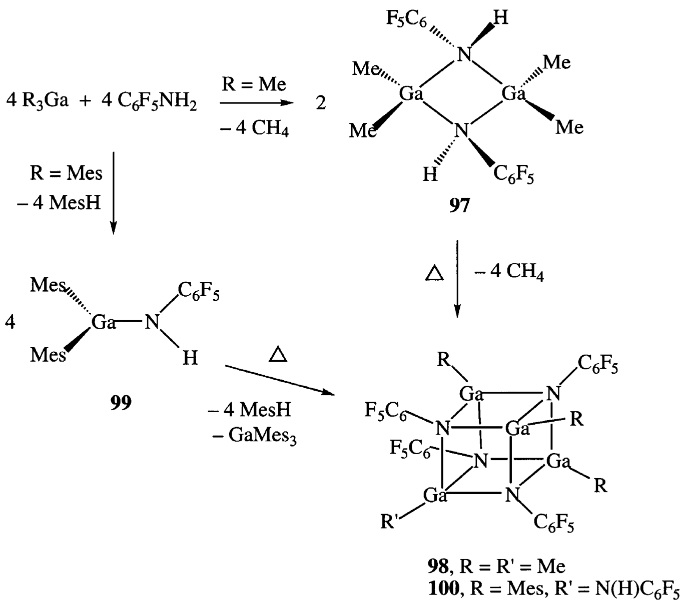


95

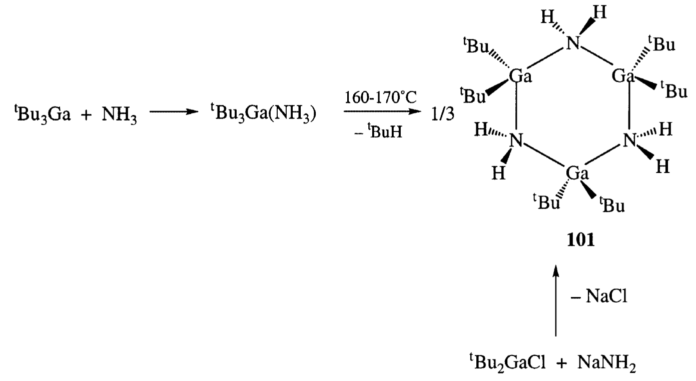


96

Some related reactions between $[R_3Ga]$ and pentafluoroaniline ($C_6F_5NH_2$) have been reported, according to Scheme 6 [49a]. Thus, the reaction between $[Me_3Ga]$ and $C_6F_5NH_2$ resulted in the initial formation of the aminogallane $[Me_2GaN(H)C_6F_5]_2$ (**97**). On heating compound **97** to 200 °C for 3 h the iminogal-



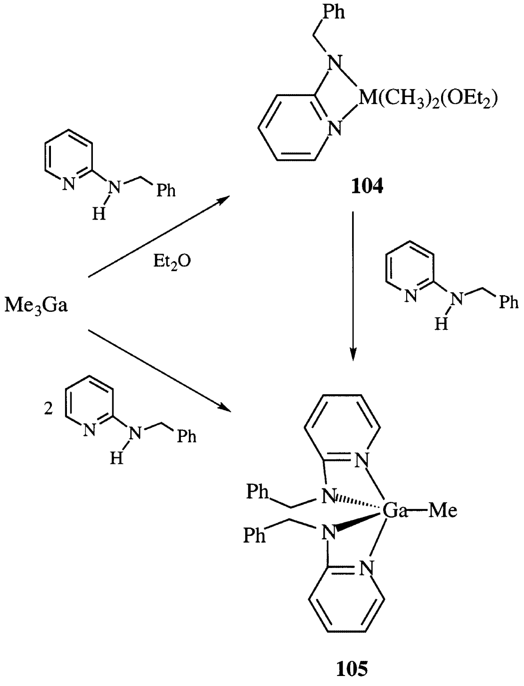
Scheme 6.



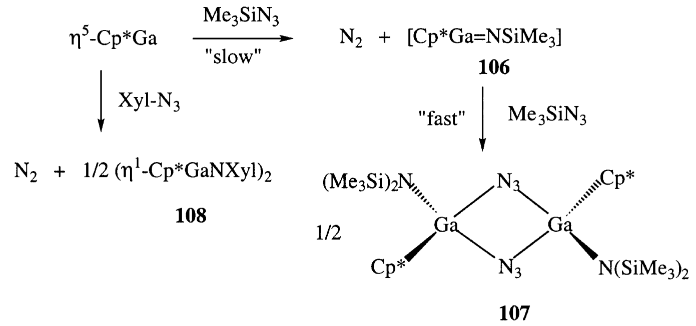
Scheme 7.

lane complex $[MeGaNC_6F_5]_4$ (**98**) was formed. The structure of **98** was determined and showed that the complex is a tetramer with a cubic Ga_4N_4 framework (cf. compound **11**). Similarly, the reaction between $[Mes_3Ga]$ and $C_6F_5NH_2$ resulted in the formation of $[Mes_2GaN(H)C_6F_5]_2$ (**99**) [49b]. Compound **99** was thought to be monomeric from mass spectral data. In contrast to **97**, thermolysis of **99** afforded $[\{C_6F_5N(H)\}Ga(MesGa)_3(\mu_3\text{-}NC_6F_5)_4]$ (**100**) rather than the expected imido complex $[MesGaNC_6F_5]_4$. The crystal structure of **100** comprises a Ga_4N_4 core with the N–Ga–N angles being more acute (85–89°) than the Ga–N–Ga angles which are greater than 90°. It is interesting that one gallium atom is coordinated to a C_6F_5NH amide rather than a mesityl ligand.

In contrast to the formation of the dimeric complexes **52**–**54** and **62**–**80**, the reaction of $[{}^t\mathrm{Bu}_3\mathrm{Ga}]$ with NH_3 or $[{}^t\mathrm{Bu}_2\mathrm{GaCl}]$ with $NaNH_2$ resulted in the isolation of the trimeric species $[{}^t\mathrm{Bu}_2\mathrm{GaNH}_2]_3$ (**101**), according to Scheme 7 [50]. The structure of compound **101** was determined and revealed a planar Ga_3N_3 core with the ^{t}BuGa groups staggered above and below this plane (N–Ga–N 106.4(1)°, Ga–N–Ga 134.5(3)°). The coordination geometry at each gallium atom is approximately tetrahedral with Ga–N bond distance of 2.017(2) Å. A similar trimeric complex was isolated from the reaction of $[Me_3Ga]$ with excess ammonia [51]. Initially the complex $[Me_3Ga(NH_3)]$ is formed, which when heated at 120 °C decomposes to yield CH_4 and the trimer $[Me_2GaNH_2]_3$ (**102**). The crystal structure of **102** revealed that in the Ga_3N_3 ring four consecutive ring atoms are coplanar (Ga–N 1.93(2)–2.05(2) Å). The remaining two atoms of the ring are on the same side of the plane so the ring has a 'sofa' conformation. The internal ring angles range from 93.8(8) to 101.3(8)° at gallium and 119.5(9) to 125.3(9)° at nitrogen. The trimeric complex $[Me_2GaN(H)Me]_3$ (**103**) was reported to result from the reaction of Me_3Ga and $MeNH_2$ [39a]. However, the same reaction carried out at 210 °C, was reported 25 years ago to result in the formation of the polyiminogallane $[(MeGaNMe)_6(Me_2GaNHMe)_2]$ [52].



Scheme 8.



Scheme 9.

The reaction of 2-benzylaminopyridine with [Me_3Ga] resulted in the formation of [$Me_2Ga\{2\text{-}[N(CH_2C_6H_5)]NC_5H_4\}(OEt_2)$] (**104**), according to Scheme 8 [53]. The identification of **104** was confirmed by ^1H-NMR and by the fact that reaction of **104** with a second equivalent of 2-[$N(CH_2C_6H_5)$]NC_5H_4 resulted in the isolation of [$MeGa\{2\text{-}[N(CH_2C_6H_5)]NC_5H_4\}_2$] (**105**). Compound **105** can also be prepared from the direct reaction of [Me_3Ga] with 2 equiv. of 2-[$N(CH_2C_6H_5)$]NC_5H_4. The monomeric nature of the bisamide **105** was confirmed by X-ray diffraction and revealed an unusual distorted square-based pyramidal coordination geometry of the gallium centre (amido N–Ga–N 113.2(1)°). As expected, the Ga–N(amido) bond distances are slightly shorter than the Ga–N(py) bond lengths (1.933(3) vs. 2.226 Å).

A further synthetic approach to the formation of compounds of type [$R_2GaN(R')R''$]$_n$ ($R = Me$, $R' = H$, $R'' = H$, Me, ^{t}Bu, Cy; $R = Me$, $R' = Me$, $R'' =$ Ph, Cy; $R = Me$, $R' = R'' = Et$; $R = Et$, $R' = H$, $R'' = Me$, ^{t}Bu; $R = R' = R'' = Et$) involves the elimination of cyclopentadiene from the reaction of [R_2GaCp] with the corresponding amine [54]. All the compounds can be prepared in high yields; however, no structural information is available.

A novel approach for the generation of dimeric monoamidogallanes has been recently reported [55]. Thus, the reaction of [η^5-Cp*Ga] with Me_3SiN_3 resulted in the formation of the dimeric azide-bridged gallane [$(\eta^1\text{-}Cp^*)Ga(\mu\text{-}N_3)\{N(SiMe_3)_2\}$]$_2$ (**107**), as summarised in Scheme 9 [55]. Compound **107** can be formally regarded as the product of 'azidosilylation' of the iminogallane [Cp*Ga = $NSiMe_3$] (**106**) generated in the first step of the sequence. However, evidence for the presence of **106** could not be obtained even when only 1 equiv. of Me_3SiN_3 was added very slowly to a dilute solution of [Cp*Ga]. Therefore, it was presumed that the second reaction step is much faster than the first one.

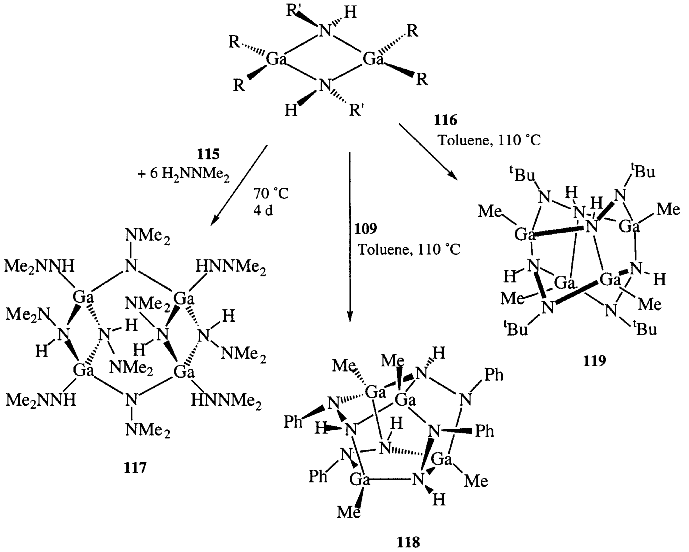
The dimeric nature of **107** was confirmed by X-ray diffraction and revealed a planar Ga_2N_2 core. The Ga–N(amido) bond distance of 1.872(2) Å is similar to those observed in the monomeric complexes **43**–**46** [24,31]. The nitrogen atoms of the bis(trimethylsilyl)amino substituents in **107** are surrounded in a trigonal planar fashion. The η^1-bonded gallium exhibits a distorted tetrahedral geometry. Interestingly, when [η^5-Cp*Ga] is reacted with a different organic azide, Xyl-N_3, the dimeric iminogallane $[[(\eta^1\text{-Cp}^*)\text{GaNXyl}]_2$ (**108**) is produced suggesting that the reaction here is much faster.

A series of related hydrazidogallane complexes have also been reported. The list includes $[\text{Me}_2\text{Ga}\{\text{N(H)N(H)Ph}\}]_2$ (**109**) [56], $[\text{R}_2\text{Ga}\{\text{N(H)NPh}_2\}]_2$ (R = Me (**110**) or Et (**111**)) [57], $[\text{R}_2\text{Ga}\{\text{N(H)NMe}_2\}]_2$ (R = Me (**112**), Et (**113**), ^{i}Pr (**114**) or H (**115**)) [58,59] and $[\text{Me}_2\text{Ga}\{\text{N(H)N(H)}^t\text{Bu}\}]_2$ (**116**) [57,60]. The structures of **109**, **110**, **114** and **115** have been determined and as expected they are similar to the dimeric structures described above in that the Ga_2N_2 cores are planar with a *trans* arrangement of the NR_2 substituents. As shown in Scheme 10, compound **117** was obtained by refluxing a solution of **115** in H_2NNMe_2 for 4 days [59]. The structure of **117** comprises two Ga_2N_2 rings bridged by NNMe_2 groups.

The tetrameric compound $[\text{MeGa}\{\text{N(H)NPh}\}]_4$ (**118**) was obtained via methane elimination from **109** after further heating (Scheme 8). The structure of **118** consists of a tetrameric unit in which the geometry about each gallium centre is distorted tetrahedral. A related tetrameric complex $[\text{MeGa}\{\text{N(H)N}^t\text{Bu}\}]_4$ (**119**) was obtained by refluxing **116** in toluene for 36 h [58]. The core structure of **119** is similar to the aryl derivative **118** and can be thought of as two hexagonal rings in the boat conformation, bound together by four-dative bonds.

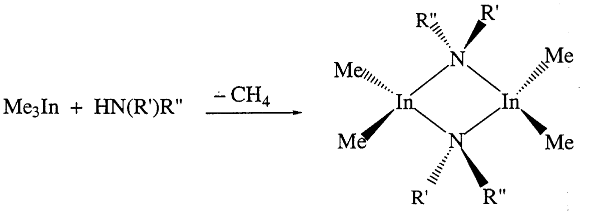
2.2. Indium

In comparison to monoamido complexes of gallium the analogous indium compounds have received less attention. At present, most of the monoamidoindium compounds that have been structurally characterised are dimeric. The first dialkylindium monoamide was prepared using the methodology shown in Eq. (3),



Scheme 10.

where $[Me_3In]$ was reacted with Me_2NH resulting in the formation of $[Me_2InNMe_2]_2$ (**120**) [61]. Further work on a series of compounds of type $[Me_2In\overline{N(CH_2)_nC}H_2]_2$ ($n = 1$ (**121a**), 2 (**121b**), 3 (**121c**) and 4 (**121d**)) showed that in solution the first member (**121a**) was trimeric, but the others (**121b–d**) were dimers [46]. The related compounds, $[Me_2In\overline{N(CH_2)_2N(Me)CH_2C}H_2]_2$ (**122**), $[Me_2In(dmp)]$ (**123**), $[Me_2InN(Me)Ph]_2$ (**124**) and $[Me_2InN(H)Ar']$ (**125**, $Ar' =$ biphenyl) were prepared in a similar manner [47,62]. Alternatively, compound **122** can be prepared via the reaction between $[Me_2InCl]$ and $Li\overline{N(CH_2)_2N(Me)CH_2C}H_2$. The structures of **120**, **121d**, **122** and **124** are similar in that they are all dimeric with a central planar In_2N_2 unit. The internal ring angles range from 84.7(3) to 85.7(4)° at indium and 94.3(3) to 95.3(2)° at nitrogen. The In–N bond distances are all similar and range from 2.22 to 2.282 Å.



120: R' = R'' = Me

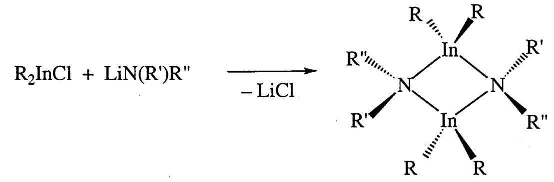
121: N(R')R'' = $\overline{N(CH_2)_nC}H_2$
a, n = 1; **b**, n = 2; **c**, n = 3; **d**, n =4

122: N(R')R'' = $\overline{N(CH_2)_2N(Me)CH_2C}H_2$
123: N(R')R'' = dmp
124: R' = Me, R'' = Ph
125: R' = H, R'' = biphenyl

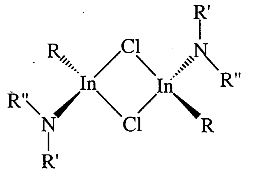
The reaction between $[Me_3In]$ and $C_6F_5NH_2$ resulted in the formation of the dimeric complex $[Me_2InN(H)C_6F_5]_2$ (**126**) [49]. The iminoindane $[MeInC_6F_5]_4$ (**127**) was formed when compound **126** was heated to 220 °C for 1 h. The structure of **127** is similar to the gallium analogue (**98**) and consists of a slightly distorted cube of alternating In and N atoms (avg. N–In–N 84.3(4)°; avg. In–N–In 95.5(4)°). The angles between the In and N atoms in **127** deviate even more from those of an ideal cube than in **98**. This was attributed to the differences in the size of the metals and to the fact that the degree of hybridisation decreases with increasing atomic mass. The In–N bond distances range from 2.167 to 2.227 Å and are similar to those observed in the aforementioned dimeric indium monoamides. Interestingly, the related complex $[MeInN^tBu]_4$ (**128**) was prepared from the reaction between $[MeInCl_2]$ and 2 equiv. of $LiN(H)^tBu$ [63]. The structure of **128** is similar to **127** and consists of a cubic In_4N_4 skeleton with an average In–N bond distance of 2.195 Å. The internal framework angles are 86.81° at indium and 93.52° at nitrogen. Other related polynuclear indium–nitrogen compounds that have been reported include $[Me(thf)InNC_6H_4F\text{-}4]_4$, $[XInN^tBu]_4$ ($X = Cl$, Br and I) and $[In_3Br_4(N^tBu)\{N(H)^tBu\}_3]$ [64,65].

The majority of monoamidoindium compounds have been prepared using standard salt elimination routes Eqs. (1) and (2). Thus, the reaction of [R_2InCl] with 1 equiv. of LiN(R′)R″ resulted in the formation of dimeric complexes of type [$R_2InN(R')R''$]$_2$ (R = Me, R′ = R″ = Cy (**129**), Et (**130**), ^{i}Pr (**131**), $SiMe_3$ (**132**) or $GeMe_3$ (**133**) [66,67]; R = Et, R′ = R″ = Et (**134**) or $SiMe_3$ (**135**) [68]; R = ^{i}Pr, R′ = H, R″ = ^{t}Bu (**136**) R = CH_2Ph, R′ = H, R″ = ^{t}Bu (**137**) [69a,69c], R = ^{t}Bu, R′ = R″ = Me (**138**) [70]). X-ray crystallographic studies on **130**–**133**, **136** and **137** revealed that they are all nitrogen bridged dimers with a planar In_2N_2 core. The internal ring angles vary depending on the size of the substituents present on the indium and nitrogen atoms (Table 1). For example, in compound **132**, the In_2N_2 core adopts a square geometry. In contrast, the internal ring angles in **136** are 83.1(1)° at indium and 96.9(1)° at nitrogen. The In–N bond distances range from 2.234(3) to 2.304(5) Å with compound **132** possessing the longest In–N bond length.

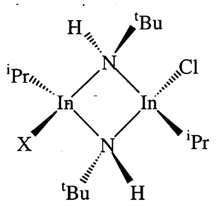
The reaction of [$RInCl_2$] with $LiN(SiMe_3)_2$ resulted in the formation of chloro-bridged dimers of type [$RIn(\mu\text{-}Cl)N(SiMe_3)_2$]$_2$ (R = CH_2Ph (**139**) or Mes (**140**) [69]. However, a 1:1 mixture of $^{i}Pr_2InCl$/$^{i}PrInCl_2$ with LiN(H)^{t}Bu leads to all three possible compounds, namely [^{i}Pr(Cl)InN(H)^{t}Bu]$_2$ (**141**), [$^{i}Pr_2In\{\mu\text{-}N(H)^{t}Bu\}_2$-In(Cl)^{i}Pr] (**142**) and [$^{i}Pr_2InN(H)^{t}Bu$]$_2$ (**136**) being produced [69]. The structure of **140** comprises of a chloro-bridged dimer with a planar In_2Cl_2 core. The



129: R = Me, R' = R'' = Cy
130: R = Me, R' = R'' = Et
131: R = Me, R' = R'' = ^{i}Pr
132: R = Me, R' = R'' = $SiMe_3$
133: R = Me, R' = R'' = $GeMe_3$
134: R = Et, R' = R'' = Et
135: R = Et, R' = R'' = $SiMe_3$
136: R = ^{i}Pr, R' = H, R'' = ^{t}Bu
137: R = CH_2Ph, R' = H, R'' = ^{t}Bu
138: R = ^{t}Bu, R' = R'' = Me



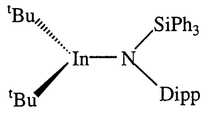
139: R = CH_2Ph, R' = R'' = $SiMe_3$,
140: R = Mes, R' = R'' = $SiMe_3$



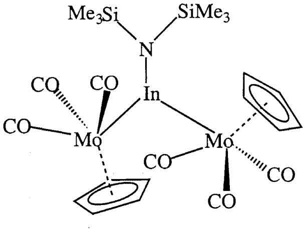
141: X = Cl
142: X = ^{i}Pr

In–N bond distances (2.020(9) Å) are similar to those observed in monomeric indium amide complexes. The structure of **142** is similar to **136** and consists of a nitrogen-bridged dimer with a planar In_2N_2 core (avg. In–N 2.214(1)°; avg. N–In–N 83.9°; avg. In–N–In 96.1(6)°). Interestingly, isomers can be detected in solutions of compounds **136**, **141** and **142**.

When bulkier substituents are present on both the In and N atoms it is possible to isolate monomeric derivatives [70–72]. Thus, the reaction between [^{t}Bu$_2$InCl] or [^{i}Pr$_2$InCl] and LiN(R′)R″ resulted in the isolation of [R_2InN(R′)R″] (R = ^{t}Bu, N(R′)R″ = N^{i}Pr$_2$ (**143**), N(SiMe$_3$)$_2$ (**144**), tmp (**145**) [71,72]; R = ^{t}Bu, R′ = Dipp, R″ = SiPh$_3$ (**146**) [71]; R = ^{i}Pr, N(R′)R″ = N^{i}Pr$_2$ (**147**), N(SiMe$_3$)$_2$ (**148**), dmp (**149**) [71]). Compounds **143**–**145** and **147**–**149** are liquids and monomeric in solution. In contrast, compound **146** is a crystalline solid. The structure of **146** has been determined and revealed a planar coordination at indium and nitrogen with a twist angle between the planes at indium and nitrogen of 15.5°. The In–N bond distance of 2.049(1) Å is relatively short in comparison to the sum of atomic radii at In and N. However, this shortening can be accounted for in terms of an ionic contribution to the In–N bond rather than the presence of significant In–N pπ–pπ bonding.



146

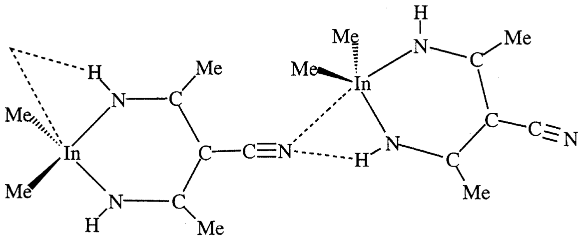


150

The reaction of [{Cp(CO)$_3$Mo}$_2$InCl] with LiN(SiMe$_3$)$_2$ leads to the formation of [{Cp(CO)$_3$Mo}$_2$InN(SiMe$_3$)$_2$] (**150**). Compound **150** is monomeric and the indium atom is coordinated in a trigonal planar manner by two [Cp(CO)$_3$Mo] fragments and a N(SiMe$_3$)$_2$ group [73]. The In–N bond distance of 2.213(3) Å in **150** is longer than that observed in **146** which is probably due to the larger size of the substituents present on the indium atom in **150**. The Mo–In–Mo bond angle is 126.6(1)° and the two N–In–Mo angles are 120.3(1) and 113.1(1)°.

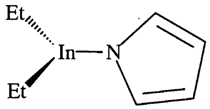
It was reported recently that MeCN can be trimerised in the presence of Me$_3$In and a trace of CsF to form [Me$_2$In{HNC(Me)}$_2$C(CN)] (**151**) [74]. The structure of **151** was determined and shows that the framework consists of a InN_2C_3 heterocycle with an average In–N bond distance of 2.204 Å (N–In–N 80.91°). In the solid-state **151** forms an infinite chain-like coordination polymeric structure via In···N contacts and N–H···N bridges. The analogous gallium complex [Me$_2$Ga{HNC(Me)}$_2$C(CN)] can also be prepared [74].

The formation of a coordination polymer has also been observed in the structures of some indium pyrrolide complexes [68,75,76]. Thus, the reaction of [Et$_2$InCl] with LiPyrr resulted in the formation of [Et$_2$InPyrr] (**152**) [68]. The structure of **152** shows an almost planar In atom with a long In–N bond distance of 2.166(4) Å. The planar pyrrole ring is tilted with respect to the coordination plane by 16.1(2)°. In

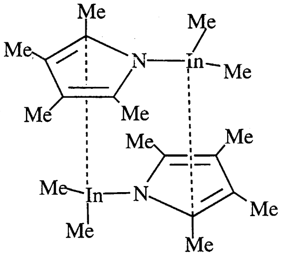


Coordination polymer of **151**

the solid state, a chain structure results via relatively short intermolecular interactions between each In atom and the double bonds of two adjacent pyrrole units. This results in the indium adopting a trigonal bipyramidal coordination geometry. Similarly, the structure of [$Me_2InPyrr$] (**153**) showed that infinite chains are formed via the linkage of Me_2In groups by the N and one carbon atom of the pyrrole ring [75]. Interestingly, compound **153** has the longest In–N bond length, at 2.335 Å, known to date.



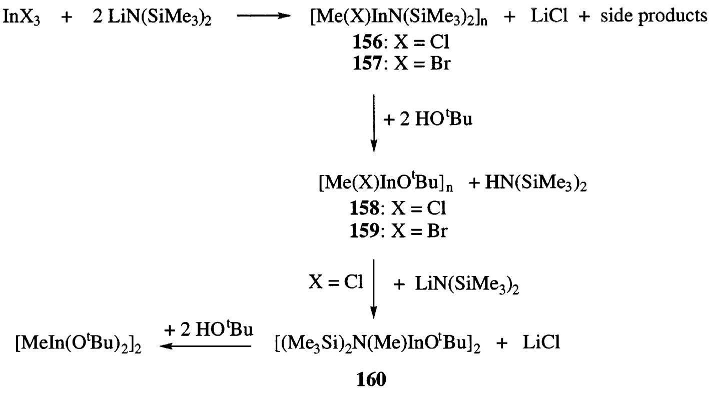
152: $Et_2InPyrr$ unit



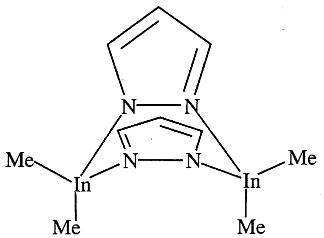
'π-dimers' in **154**

The synthesis and characterisation of a related complex incorporating a substituted pyrrole ligand has also been reported [76]. The reaction of [Me_3In] with HNC_4Me_4 resulted in the formation of [$Me_2In(NC_4Me_4)$] (**154**). The structure of **154** is similar to that of **152** and **153** in that the indium centre adopts a trigonal planar coordination geometry (In–N 2.197(3) Å). Furthermore, in the solid-state structure **154** forms 'π-dimers' via short intermolecular In···C contacts of 2.575 Å. The related complex [$Me_2InN_2C_3H_3$]$_2$ (**155**) was prepared from the reaction between [Me_3In] and pyrazole [77]. The dimeric nature of **155** was confirmed by X-ray diffraction and revealed that the In–(–N–N–)$_2$–In skeleton has a boat conformation. The In–N bond distances range from 2.197(5) to 2.227(5) Å and the N–In–N angles vary from 92.5(2) to 95.3(2)°.

The reaction of InX_3 with 2 equiv. of $LiN(SiMe_3)_3$ was reported to result in the formation of [$Me(X)InN(SiMe_3)_2$]$_n$ (X = Cl (**156**) or Br (**157**)) via methyl-group transfer onto the indium centre, according to Scheme 11 [78]. Unfortunately, no structural data are available for **156** or **157**; however, the reactivity of both compounds with alcohols has been investigated. For example, the reaction of



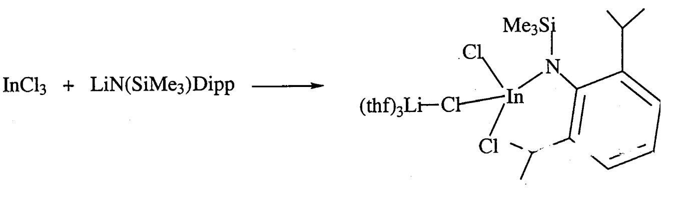
Scheme 11.



155

compounds **156** or **157** with 2 equiv. of HO^{t}Bu resulted in the isolation of [Me(X)In(O^{t}Bu)]$_2$ (X = Cl (**158**) or Br (**159**)). The desired amido complex could then be formed by reacting **158** with LiN(SiMe$_3$)$_3$. The structure of **160** was determined and reveals an oxygen-bridged dimer with a planar In_2O_2 unit. The indium atoms possess a highly distorted tetrahedral coordination sphere. The In–N bond length (2.093(4) Å) is within the range described above for the monomeric complex **146**. The amido group in **160** can be replaced by an alcohol to form [MeIn(O^{t}Bu)$_2$]$_2$ in a 60% yield.

In comparison to the formation of **146**, when InCl$_3$ was reacted with LiN(SiMe$_3$)Dipp the ionic complex [Li(thf)$_3$][Cl$_3$InN(SiMe$_3$)Dipp] (**161**) was formed [79]. The core of the structure consists of an indium centre that is tetrahedrally coordinated by three Cl atoms and one N(SiMe$_3$)Dipp ligand (In–N 2.054(2) Å). One of the chlorine atoms bridges the indium to a lithium cation whose tetrahedral

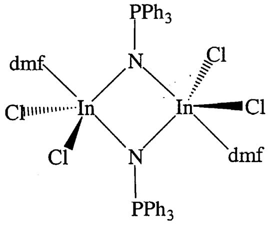


161

coordination sphere is completed by three thf molecules. In the same report, $InCl_3$ was reacted with Et_2NSiMe_3 resulting in the formation of $[Cl_2InNEt_2]_2$ (**162**) which was thought to be dimeric from the spectroscopic data.

Monoamidoindium complexes can also be prepared from stannylamines. Thus, $N(SnMe_3)_3$ reacts with $[R_2InCl]$ (R = Me, Et) with the elimination of $RSnMe_3$ and formation of the dimeric complexes $[R(Cl)InN(SnMe_3)_2]_2$ (**163**, R = Me; **164**, R = Et) [80]. Alternatively, the reaction between $[Me_2SnNR]_3$ and $[Me_3In]$ resulted in the isolation of $[Me_2InN(R)SnMe_3]_2$ (**165**, R = Me; **166**, R = ^{i}Pr), according to Scheme 2 [22]. Another approach based on $[RSnMe_3]$ elimination, involves the photoinduced reactions of $[^tBu_3In]$ with $[Et_2NSnMe_3]$ and $[^nBu_2NSnMe_3]$ [81]. The two complexes, $[^tBu_2InNEt_2]_2$ (**167**) and $[^tBu_2InN^nBu_2]_2$ (**168**), were isolated from the aforementioned reaction along with other products. The crystal structures of **163**–**168** are similar in that they are nitrogen-bridged dimers. The central In_2N_2 unit is planar in all the complexes except **167** and **168**. This results in the internal ring angles in compounds **163**–**168** ranging from 83.6(1) to 89.9(7)° for N–In–N and from 90.1(2) to 96.2(2)° for In–N–In. As expected, the substituents on the In and N centres adopt mutually *trans* arrangements.

A related phosphoraneiminato complex $[Cl_2(dmf)In(NPPh_3)]_2$ (**169**) was prepared via the reaction of $InCl_3$ with $Ph_3PNSiMe_3$ in the presence of dmf [82]. The X-ray crystal structure of **169** comprises dimeric molecules in which the $NPPh_3$ groups act as bridging ligands. The pentacoordinate indium centre adopts a distorted trigonal bipyramidal geometry (axial In–N 2.179(2) Å; equatorial In–N 2.112(4) Å).



169

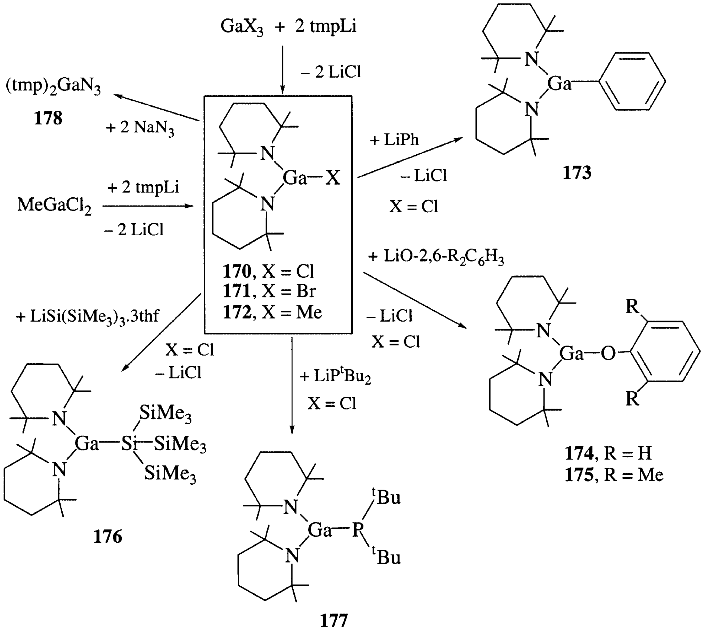
3. Diamides

Gallium and indium diamides have received little attention and only a few examples have been structurally characterised. Many of the complexes have been prepared using standard salt elimination routes, as described in detail below.

3.1. Gallium

A series of diamidogallanes of type $[XGa(tmp)_2]$ (X = Cl (**170**), Br (**171**), Me (**172**), Ph (**173**), OPh (**174**), O-2,6-$Me_2C_6H_3$ (**175**) [30], $Si(SiMe_3)_3$ (**176**) [83], $P(^tBu)_2$ (**177**) [84] and N_3 (**178**) [85]), have been reported, as summarised in Scheme 12. The X-ray crystal structures of **173**, **174**, **176** and **177** revealed that the gallium centre in all the compounds adopts a trigonal planar geometry. The N–Ga–N angle varies depending on the substituents present on the gallium centre. Thus, the N–Ga–N bond angle in **173** and **174** is 129.0(1) and 133.9(1)°, respectively. In contrast, in **176** and **177** this angle is more acute at 121.8° due to the presence of the $-\mathrm{Si(SiMe_3)_3}$ and $-\mathrm{P}({}^t\mathrm{Bu})_2$ groups, respectively. They are all monomeric and the geometry around the nitrogen atom is planar, although in **174** one of the nitrogen atoms shows a slightly pyramidal coordination geometry. The result of this is that the two Ga–N bond distances in **174** are quite different (Ga–N 1.849 and 1.818 Å). The Ga–N bond distance of 1.91 Å in **176** is long compared to those observed in **173** (Ga–N 1.883(2) Å) and **174** (avg. Ga–N 1.834 Å). This is probably a result of the presence of the bulky $-\mathrm{Si(SiMe_3)_3}$ group on the gallium centre.

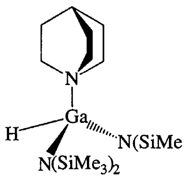
The reduction of **170** with Na/K resulted in the formation of $[\mathrm{Ga_2(tmp)_4}]$ (**179**) [86]. The crystal structure of **179** shows the presence of a Ga–Ga bond [Ga–Ga 2.525(1) Å] with the two $\mathrm{GaN_2}$ units twisted by 31° from each other (avg. N–Ga–N 118.6°). The Ga–N bond distance of 1.901(4) Å is similar to that observed in **176** (Ga–N 1.91 Å). The diphosphandiylbisgallane complex, $[\mathrm{(tmp)_2GaP}{}^t\mathrm{Bu}]_2$ (**180**), was prepared in a similar manner to **177** and possesses pyramidal phosphorus atoms (Ga–P 2.423 Å) [84]. The P–P bond length of 2.254(1) Å in **180** is consistent with a P–P single bond. The coordination geometry of the gallium centres in **180** are distorted trigonal planar with N–Ga–N bond angles of 121.38(8)°. Interestingly, the reaction of **170** with potassium thiocyante did not result in a simple substitution product of the halide [87]. However, the heterocubane $[\mathrm{(tmp)GaS}]_4$ was formed via elimination of the cyanamide tmp–CN.



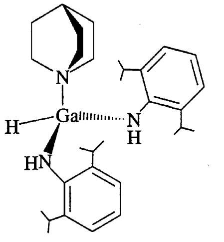
Scheme 12.

The quinuclidine-stabilised amidogallanes [HGa{N(SiMe$_3$)$_2$}$_2$(quin)] (**181**) and [HGa{N(H)Dipp}$_2$(quin)] (**182**) were synthesised from the reaction of [HGaCl$_2$(quin)] with LiN(R)R′ (R = R′ = SiMe$_3$ or R = H, R′ = Dipp) [11]. Compounds **181** and **182** are monomeric with the gallium atoms adopting distorted tetrahedral geometries. Compound **181** has a larger N–Ga–N angle than **182** due to steric reasons (**181**, N–Ga–N 119.41(6)°; **182**, N–Ga–N 109.89(7)°). The average Ga–N(amido) bond distances are slightly shorter in **182** (avg. Ga–N 1.901(2) Å) than those observed in **181** (avg. Ga–N 1.9226 Å). The geometry at the N(amide) atom in **181** is almost planar whereas in **182** the amido nitrogen atoms are more pyramidal (343 and 350°). The two diisopropylphenyl groups in **182** are orientated away from the quinuclidine ligand such that the planes of the groups are approximately parallel to one another.

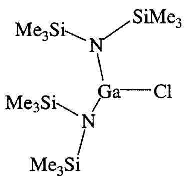
Salt elimination routes were also used to prepare [Mes*Ga{N(H)Ph}$_2$] (**183**) and [ClGa{N(SiMe$_3$)$_2$}$_2$] (**184**) via the reaction of [RGaCl$_2$] and LiN(R′)R″ [31]. The crystal structures of **183** and **184** showed that both compounds are monomeric. The gallium and nitrogen centres have trigonal planar coordination with a N–Ga–N angle of 105.3(4)° in **183** and 128.5(2)° in **184** due to the different sizes of the substituents on the Ga and N centres. The Ga–N distances range from 1.834(4) to 1.842(4) Å. There are close approaches between hydrogens from the *o*-^{t}Bu groups and gallium (Ga···H 2.37 Å) in compound **183**. In contrast to the formation of **184**, the reaction between GaCl$_3$ and LiN(SiMe$_3$)Dipp resulted in the formation of [{(Dipp(Me$_3$Si)N}Ga(Cl){NDipp(SiMe$_2$)N(SiMe$_3$)Dipp}] (**185**) [28]. The two Ga–N bond distances in **185** are 1.858(3) and 1.845(3) Å. The N–Ga–N bond angle of 137.2(2)° is large due to the bulky substituents on the nitrogen atoms.



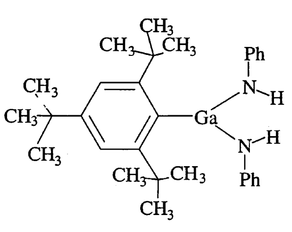
181



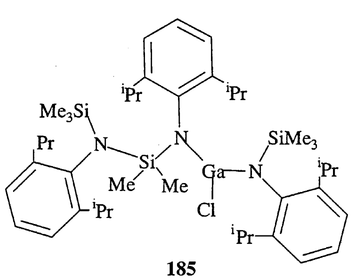
182



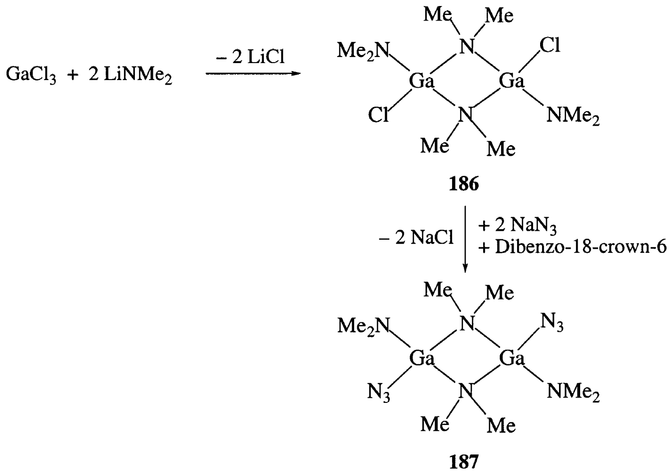
184



183



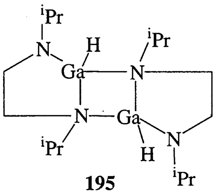
185



Scheme 13.

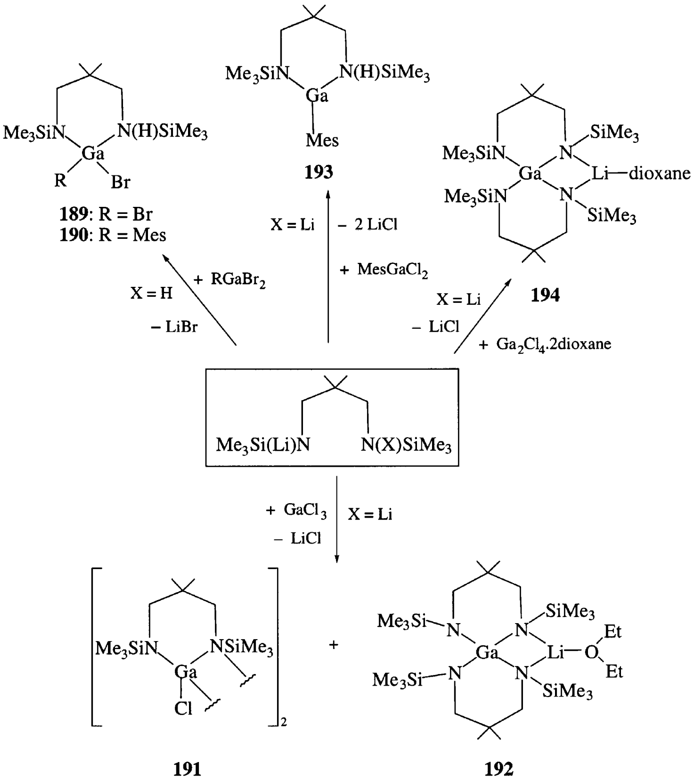
The synthesis of some dimeric diamidogallanes have also been reported via salt elimination routes [17,27,85], as shown in Scheme 13. The crystal structures of $[Cl\{Me_2N\}Ga\{\mu\text{-}NMe_2\}]_2$ (**186**) and $[N_3\{Me_2N\}Ga\{\mu\text{-}NMe_2\}]_2$ (**187**) are similar in that they are both dimeric with bridging NMe_2 groups and a planar Ga_2N_2 core. However, in the solid-state compound **187** consists of a polymeric chain of dimers with the azide moiety bridging two gallium centres on neighbouring dimers. Compound **187** was shown to deposit epitaxial single crystalline films of GaN at 580 °C. Interestingly, when **187** is reacted with pyridine the gallium tris(azide) complex $[Ga(N_3)_3(py)_3]$ is produced [88]. The related complex $[N_3Ga\{N(Et)\text{-}CH_2CH_2NMe_2\}_2]$ (**188**) was prepared in a similar manner to **187** [85]. Unfortunately, no structural data are available for compound **188**.

The synthesis and characterisation of some cyclic compounds of gallium incorporating the 2,2-dimethyl-1,3-bis[(trimethylsilyl)amino]propane ligand have been reported, according to Scheme 14 [89]. The reaction of 2,2-dimethyl-*N*-lithio-1,3-bis[(trimethylsilyl)amino]propane with $[RGaBr_2]$ resulted in the isolation of the cyclic monomeric amine(amino)gallanes **189** ($R = Br$) and **190** ($R = Mes$) [89]. The cyclic bis(amino)gallane **191** and **193** were prepared by the reaction of the dilithio amine $[Me_3SiN(Li)CH_2C(Me_2)CH_2N(Li)SiMe_3]$ with $GaCl_3$ and $[MesGaCl_2]$, respectively. However, the reaction producing compound **191** is accompanied by the formation of the tetra(amino)gallate (**192**). Compound **194**, which is very similar to **192**, was formed by reaction of the dilithio amine with $Ga_2Cl_4 \cdot 2$dioxane. The crystal structures of **189**, **191** and **192** have been determined. The structure of **189** consists of a six-membered C_3GaN_2 ring skeleton with a twist conformation and a distorted tetrahedral gallium atom. Compound **189** has one short Ga–N single bond (1.84 Å) and a longer Ga–N dative bond (2.04 Å) with one nitrogen planar and the other distorted tetrahedral. The N–Ga–N and Br–Ga–N angles are 99.9(5) and 116°, respectively. The bis(amino)gallium chloride **191** crystallises as a dimer and exhibits a central asymmetrical four-membered Ga_2N_2 ring with *syn*-orientated subsitutents. The Ga–N bond distances associated with the Ga_2N_2 ring are 1.994 and 2.056 Å. As expected, the terminal Ga–N bond lengths are shorter at 1.843 Å. In the solid-state structure of **192** two nitrogen atoms bridge the Li and Ga centres. In addition, there are two Li–H (from the ethyl groups) contacts completing the coordination sphere at the Li atom. The related dimeric cyclic bis(amino)gallane $[\mathrm{HGa}\{(^{i}\mathrm{Pr})\mathrm{NCH_2CH_2N}(^{i}\mathrm{Pr})\}]_2$ (**195**), has also been reported [90].



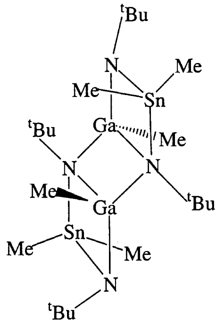
195

The reaction between diazadistannetidine $[\mathrm{Me_2SnN^{t}Bu}]_2$ and $[\mathrm{Me_3Ga}]$ resulted in the isolation of $[\mathrm{Me_2Sn(N^{t}Bu)_2GaMe}]$ (**196**) in low yield [91]. The structure of **196** comprises a centrosymmetric dimer with three consecutive four-membered rings.



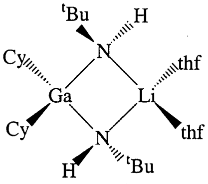
Scheme 14.

The central Ga_2N_2 unit is formed by two Ga←N dative bonds of 2.037 Å. The N–Ga–N and Ga–N–Ga internal ring angles are 86.1(1) and 93.9(1)°, respectively. The two SnN_2Ga rings and the central ring form angles of ±113.7°.

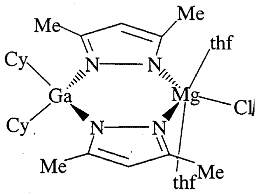


196

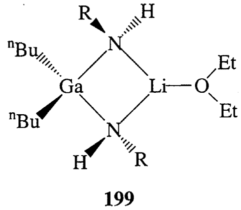
A number of diamidogallate complexes have also been reported [37,92]. The reaction of 2 equiv. of $LiN(H)^tBu$ with $[Cy_2GaCl]_2$ produced the gallate complex $[Cy_2Ga\{\mu\text{-}N(H)^tBu\}Li(thf)_2]$ (**197**) [92]. Similarly, the reaction of 2 equiv. of Li(3,5-Me_2Pz) with $[Cy_2GaCl]_2$ resulted in the isolation of the gallate species $[Cy_2Ga(\mu\text{-}3,5\text{-}Me_2Pz)MgCl(thf)_2]$ (**198**) [92]. An X-ray crystallographic study shows that the amide ligands in **197** and **198** bridge from the Ga atom to Li^+ or $MgCl^+$, respectively. The Ga–$(N)_2$–Li four-membered ring in **197** is planar with N–Ga–N and Ga–N–Ga angles of 89.1(5) and 86.3(8)°, respectively. The two Ga–N bond lengths in **197** are 1.99(2) Å. The structure of **198** consists of two pyrazolyl groups bridging the Ga and Mg atoms through adjacent pyrazolyl nitrogens. The Ga–N bond lengths in **198** are 2.009(6) and 2.020(5) Å which are similar to those found in **197**. The coordination geometry around the magnesium is trigonal bipyramidal and the Ga–$(N–N)_2$–Mg six-membered ring is planar. The related reaction of $[^nBu_2GaCl]$ with 2 equiv. of $LiNH(2,6\text{-}Me_2C_6H_3)$ resulted in the formation of $[^nBu_2Ga\{\mu\text{-}N(H)2,6\text{-}Me_2C_6H_3\}Li(OEt_2)]$ (**199**) [37]. The structure of **199** is similar to that of **197** with the amido groups bridging the Ga and Li centres.



197



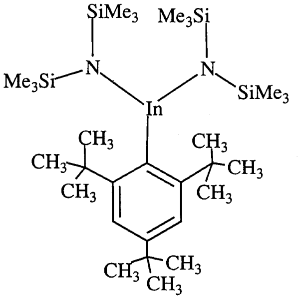
198



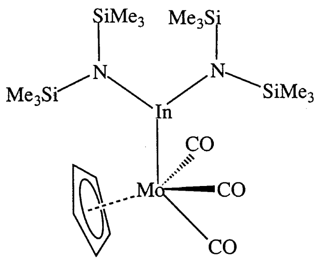
199

3.2. Indium

Treatment of [(R)InX_2] with 2 equiv. of $LiNR'_2$ (R = X = Br, NR'_2 = tmp; R = Mes*, X = Cl, R′ = $SiMe_3$) resulted in the isolation of the indium diamides [$(tmp)_2InBr$] (**200**) and [Mes*In{$N(SiMe_3)_2$}$_2$] (**201**) [25,93]. The monomeric nature of **201** was confirmed by X-ray diffraction and revealed that the indium and nitrogen centres have an essentially planar coordination geometry. The In–N bond distances are 2.094(4) and 2.103(2) Å and the N–In–N angle is 119.4(2)°. A related bis(amide) complex [{Cp$(CO)_3$Mo}In{$N(SiMe_3)_2$}$_2$] (**202**) has been prepared by the reaction of [{Cp$(CO)_3$Mo}InCl_2] with 2 equiv. of $LiN(SiMe_3)_2$ [73]. The structure of **202** is monomeric and contains an indium atom in a trigonal planar coordination geometry (N–In–N 116.6(3)°; N–In–Mo 117.3(1) and 129.5(1)°). The bond lengths and angles around indium in **202** are similar to those observed in **201** (In–N 2.096(3) Å).

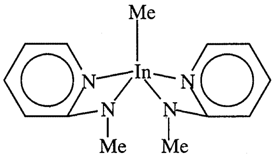


201

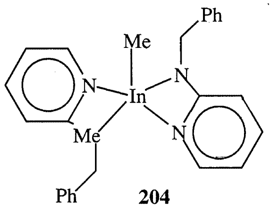


202

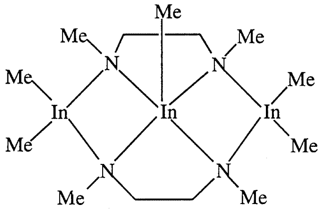
The reaction between [Me_3In] and 2 equiv. of 2-(methylamino)pyridine [N(Me)C_5H_4N] or 2-(benzylamino)pyridine [N($CH_2C_6H_5$)C_5H_4N] resulted in the formation of [MeIn{N(Me)C_5H_4N}$_2$] (**203**) and [MeIn{N($CH_2C_6H_5$)C_5H_4N}$_2$] (**204**), respectively [53,62,94]. In contrast, treatment of [Me_2InCl] with mono-*N*-lithiated-*N*,*N*′-dimethylethylenediamine gave [MeIn{MeN$(CH_2)_2$NMe}InMe_2]$_2$ (**205**) [62,94]. The structures of **203**–**205** show that they are all monomeric in the solid state. In compounds **203** and **204**, the central indium centre is in a distorted square-based pyramidal environment with the base formed by the two diamide ligands and a methyl-group apical (**203**, amido N–In–N 113.0(2)°; **204**, amido N–In–N 115.5(1)°). In compound **204**, the two nitrogen atoms of the pyridine ligands as well as those of the amido group are orientated in a *trans* configuration. This is in contrast to **203** where the groups are arranged in a *cis* configuration. This is probably a result of the differences in size between the methyl and benzyl substituents on the amido ligands. The average In–N(amido) bond lengths in **203** and **204** are 2.140 and 2.157 Å, respectively. In compound **205** there is a central square-pyramidal indium and the base is formed by two chelating diamide ligands with a methyl-group apical. Each diamide also bridges two Me_2In units with distorted tetrahedral symmetry. Therefore, **205** is also a monodialkylamide. The average In–N(amide) bond length of 2.201 Å observed in **205** is slightly longer than those observed in **203** and **204**.



203

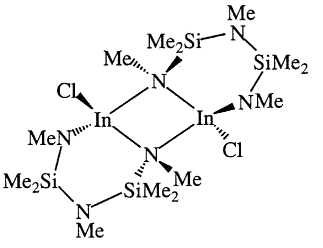


204

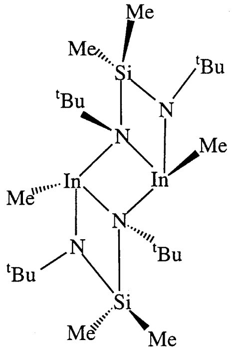


205

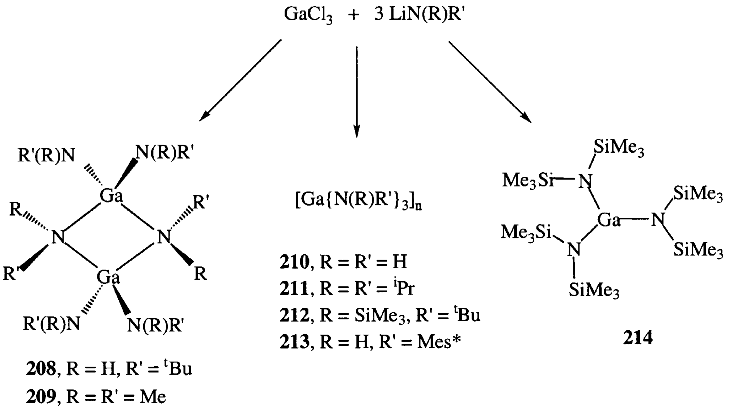
Two complexes incorporating bidentate amide ligands have also been reported [95,96]. Thus, treatment of $InCl_3$ with 1 equiv. of $[MeN(SiMe_2NMeLi)_2]$ resulted in the formation of the dimer $[ClIn\{(NMeSiMe_2)_2NMe\}]$ (**206**) [95]. The dimeric nature of **206** was confirmed by X-ray diffraction. The indium atom in **206** has a distorted tetrahedral geometry with the four coordination sites occupied by a Cl and three amide nitrogen atoms, one of which is terminal and the other two are bridging. In compound **206**, the angles around the indium vary from 90 to 116° with the smallest angle associated with the bridging amide groups. As expected, the terminal In–N bond distance (2.036(7) Å) is shorter than the bridging In–N bond lengths (avg. 2.204 Å). The related complex $[MeIn(N^tBu)_2SiMe_2]_2$ (**207**) is also dimeric in the solid state [96]. The structure of **207** comprises a polycyclic unit built up of three four-membered rings that share common edges and are orthogonal to each other. The indium centres adopt a distorted tetrahedral coordination geometry with N–In–N and In–N–In angles of 87.8(1) and 92.2(1)°, respectively. The In–N bond lengths associated with the In_2N_2 core are 2.277(2) and 2.256(4) Å and are similar to those observed in the aforementioned dimeric indium monoamides. The structure of **207** is very similar to the homologous Ga/Sn compound $[MeGa(N^tBu)_2SnMe_2]_2$ (**196**).



206



207



Scheme 15.

4. Triamides

Indium and gallium triamides have been prepared using salt elimination routes or via amine exchange.

4.1. *Gallium*

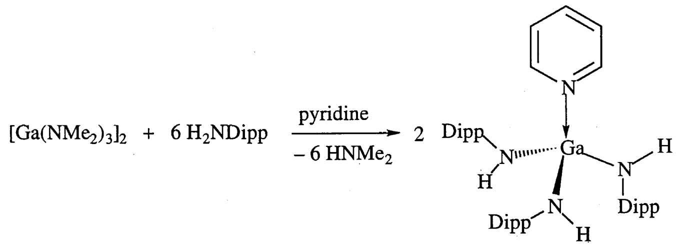
The homoleptic gallium amido compounds **208**–**214** have been prepared using standard salt elimination routes, as summarised in Scheme 15. The solid-state structure of compound **208** comprises dimers of composition $[\{^t\mathrm{Bu(H)N}\}_2\mathrm{Ga}\{\mu\text{-}\mathrm{N(H)}^t\mathrm{Bu}\}]_2$ [97]. The Ga_2N_2 ring in **208** adopts a non-planar 'butterfly' type conformation with the ^{t}Bu groups of the bridging amido substituent in mutually *cis* positions (N–Ga–N 81.6(3)°, Ga–N–Ga 94.8(4)°). The Ga–N bond distance for the bridging amido groups in **208** (2.008(8) Å) is similar to those observed for the aforementioned dimeric amidogallanes. The terminal Ga–N distance of 1.813(10) Å falls close to the estimated single-bond value of 1.84 Å if adjustment is made for ionic contributions. A similar dimeric structure was observed for compound **209** [98]. In contrast to **208**, the structure of **209** consists of a planar Ga_2N_2 ring with only minor deviations from a perfectly square configuration positions (N–Ga–N 87.7(1)°, Ga–N–Ga 92.3(1)°). The Ga–N bond distances in **209** are similar to those observed in **208** (terminal Ga–N 1.855(4) Å, bridging Ga–N 2.013(3) Å).

The gallium homoleptic amide, $[\mathrm{Ga(NH_2)_3}]_n$ (**210**), has been synthesised but not structurally characterised [99]. Compound **210** was reported to be thermally unstable. No structural data are available for compounds **211**–**213**, although **212** and **213** are thought to be monomeric from the spectroscopic data ($n = 1$) [97,100,101]. A range of gallium alkylthiolate complexes have been prepared from the reaction of **209** and **211** with thiols [100]. The crystal structure of $[\mathrm{Ga\{N(SiMe_3)_2\}_3}]$ **214** has been reported three times [17,31,97,102]. The structure of **214** is monomeric with the $(Me_3Si)_2N$ groups arranged in a propeller fashion with a dihedral angle of ~50° between the Si_2N and GaN_3 planes. The gallium and nitrogen atoms both adopt a trigonal planar geometry (N–Ga–N 120°). The Ga–N bond distances fall within the range of 1.85–1.92 Å.

The gallium triamide, $[Ga(tmp)_3]$ (**215**), has been prepared by the thermal reaction of $GaCl_3$ with 3 equiv. of Htmp, according to Eq. (8) [97]. No structural data are available for **215**; however, the equivalence of all the methyl groups in the ^1H-NMR spectrum of **215** is indicative of monomer formation.

$$\mathrm{GaCl_3 + 3Htmp \rightarrow \underset{\mathbf{215}}{Ga(tmp)_3} + 3HCl} \tag{8}$$

The reaction of 6 equiv. of H_2NDipp with **209**, followed by treatment with pyridine resulted in the formation of $[Ga\{N(H)Dipp\}_3(py)]$ (**216**) [101]. The addition of pyridine was necessary in order to isolate crystalline products. The molecular structure of **216** comprises monomeric units with the gallium centre adopting a distorted tetrahedral geometry. The average Ga–N(amido) bond distance of 1.871(8) Å is similar to that observed in compound **43**.



216

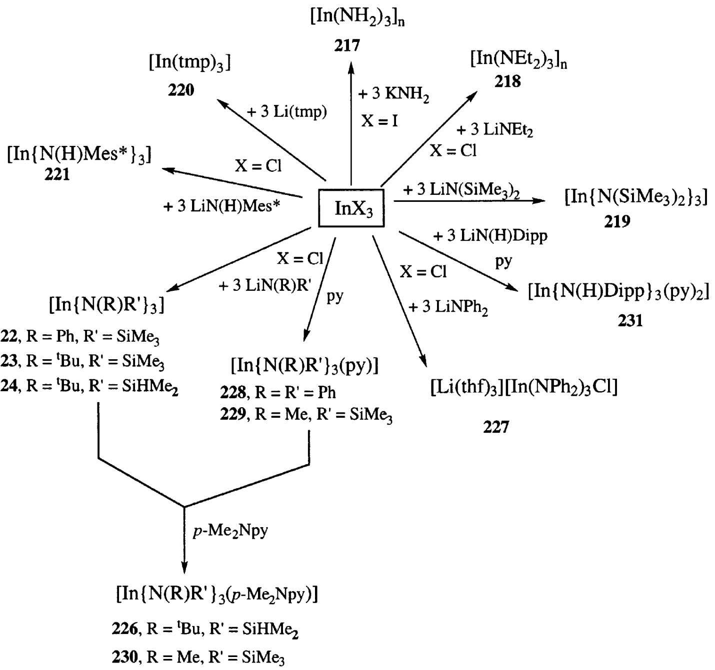
4.2. Indium

Until recently there were only two examples of homoleptic indium triamides in the literature. However, due to the interest in using homoleptic indium amido compounds as precursors to indium nitride films, there has been increased research in this area. All of the homoleptic indium amido complexes (**217**–**231**) have been prepared using salt elimination routes, as summarised in Scheme 16 [93,101–104]. Indium tris(amide), $[In(NH_2)_3]_n$ (**217**), has been synthesised from the reaction between InI_3 and 3 equiv. of KNH_2 in anhydrous liquid ammonia [103b]. Compound **217** is insoluble in NH_3 but dissolves in NH_3 solutions of KNH_2 to form potassium indium amides of type $[K_xIn(NH_2)_{3+x}]$. Indium nitride (InN) was obtained from the thermolysis of **217**; however, no structural data are available for this complex.

The crystal structures of **219**–**221** are all similar in that they are monomeric and the geometry at the indium centre in each compound is trigonal planar (N–In–N 120°) [93,101]. As expected, the In–N bond lengths in **219** (2.049(1) Å), **220** (2.08(1) Å) and **221** (2.068(7) Å) are all similar. The structure of **219** is also similar to the gallium analogue $[Ga\{N(SiMe_3)_2\}_3]$ (**214**).

A series of homoleptic indium tris(silylamides) have been synthesised as shown in Scheme 16 [104]. Compounds **222** and **224** are liquids whereas **223** is a volatile white solid. The ether adduct of **222**, $[In\{N(Ph)SiMe_3\}_3(OEt_2)]$ (**225**), was isolated as a colourless crystalline solid. Similarly, compound **224** was reacted with *p*-(dimethylamino)pyridine to form the adduct $[In\{N(^tBu)SiHMe_2\}_3(p\text{-}Me_2Npy)]$ (**226**). When the less sterically hindered amide $-NPh_2$ was reacted with $InCl_3$ in a weakly coordinating solvent, the ionic complex $[Li(thf)_4][In(NPh_2)_3Cl]$ (**227**) was isolated. In contrast to the formation of **227**, the reaction between $InCl_3$ and 3 equiv. of $LiN(R)R'$ in the presence of pyridine, resulted in the formation of the neutral complexes $[In\{N(R)R'\}_3(py)]$ (**228**, $R = R' = Ph$; **229**, $R = Me$, $R' = SiMe_3$). The pyridine ligand in compound **229** can be displaced by *p*-(dimethylamino)pyridine to yield $[In\{N(Me)SiMe_3\}_3(p\text{-}Me_2Npy)]$ (**230**). Interestingly, the reaction between $InCl_3$ and 3 equiv. of LiN(H)Dipp in the presence of pyridine resulted in the coordination of two pyridine ligands to give $[In\{N(H)Dipp\}_3(py)_2]$ (**231**) [101].

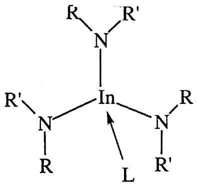
X-ray crystallographic studies show that in **225**, **226** and **228** the amide nitrogen and In atoms are close to planar. The overall geometry of the four coordinate In atoms can be loosely described as distorted tetrahedral (avg. N(amido)–In–N(amido) 118.2° (**225**), 116.0° (**226**), 124.4° (**228**)). The In–N(amide) distances in **226** (avg. 2.125(3) Å) are significantly longer than those in **225** (2.095(2) Å) and **228** (2.083(5) Å). This is probably a result of the increased steric require-



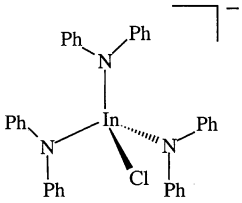
Scheme 16.

ments of the ^{t}Bu group in **226**. The structure of **227** has also been determined and the four coordinate In centre in the anion, $[In(NPh_2)_3Cl]^-$, approaches ideal tetrahedral geometry (avg. N–In–N 112.5°). The average In–N bond distance in **227** is 2.06 Å. The crystal structure of $[In\{N(H)Dipp\}_3(py)_2]$ (**231**) revealed that the pentacoordinate In centre adopts a distorted trigonal bipyramidal geometry in which the pyridine and the N(H)Dipp ligands occupy axial and equatorial positions, respectively (avg. N(amido)–In–N(amido) 116.6°). The average In–N(amide) bond distance in **231** (2.116(4) Å) is longer than those observed in **225** and **228** but similar to those in **226**. These trends can be attributed to steric effects.

The reactivity of the indium amides **218**, **223** and **226** has been investigated. For example, the reactions of these complexes with fluorinated alcohols results in the formation of indium fluoroalkoxide complexes [105].

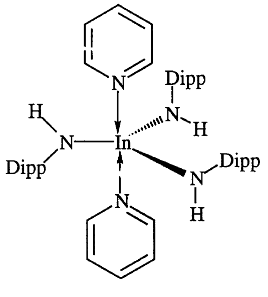


225, R = Ph, R' = $SiMe_3$, L = OEt_2
226, R = ^{t}Bu, R' = $SiHMe_2$, L = *p*-Me_2Npy
228, R = R' = Ph, L = py

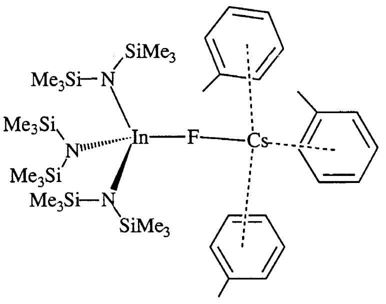


227

The synthesis of the tris-ligand complex $[In\{N(CH_2C_6H_5)C_5H_4N\}_3]$ (**232**) was reported from the reaction of $[Me_3In]$ with 3 equiv. of 2-(benzylamino)pyridine [53]. Alternatively, compound **232** could be prepared via the reaction between $[MeIn\{N(CH_2C_6H_5)C_5H_4N\}_2]$ (**204**) and 1 equiv. of 2-(benzylamino)pyridine. No structural data are available for compound **232**. The salt $[Cs(toluene)_3]$-$[FIn\{N(SiMe_3)_2\}_3]$ (**233**) has been prepared via the reaction of CsF with **219** in toluene [106]. The structure of **233** consists of a Cs^+ ion surrounded by the indate ion and three toluene molecules in a distorted tetrahedral geometry. The tetracoordinate In centre adopts a tetrahedral geometry with an average In–N bond distance of 2.125(3) Å (N–In–N 117.2(1)°). The Cs–F–In unit is almost linear [174(1)°].



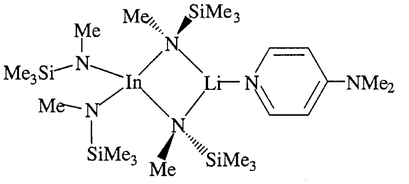
231



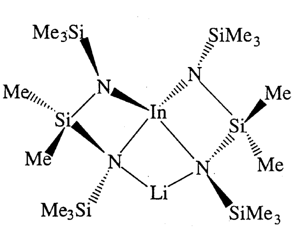
233

5. Tetraamides

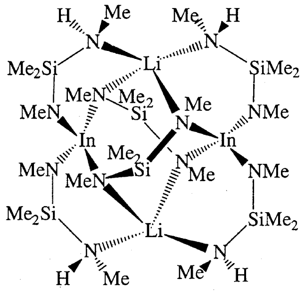
There are very few examples of tetraamido-gallium and indium complexes in the literature [73,104]. The tetraamidogallane **191** was described above (Section 3.1). The reaction of $InCl_3$ with 3 or 4 equiv. of $LiN(Me)SiMe_3$ was reported to yield the tetraamido complex $[Li(ether)][In\{N(Me)SiMe_3\}_4]$ (**234**) [104]. In order to isolate a crystalline product, compound **234** was reacted with *p*-(dimethylamino)pyridine which resulted in the formation of $[Li(p\text{-}Me_2Npy)][In\{NMe(SiMe_3)\}_4]$ (**235**). The crystal structure of **235** was investigated by X-ray diffraction and showed a severely distorted tetrahedral geometry at indium. Two of the amido groups bridge the anion and cation. The amide nitrogen coordination geometries are all planar with the exception of the two bridging nitrogens which show a slight pyramidalisation because they are bound to the Li cation. As expected, the In–N bond distance for the bridging amido groups (2.17(1) Å) is longer than those to the terminal amido groups (2.07(1) Å). The synthesis and characterisation of two tetraamido-indium compounds incorporating bidentate amide ligands have also been reported [95,107]. The reaction between $InCl_3$ and 4 equiv. of $[HNMeSiMe_2NMeLi]$ resulted in the formation of $[Li\{In(HNMeSiMe_2NMe)_2(MeNSiMe_2NMe)\}]_2$ (**236**) [95]. Reacting $InCl_3$ with 2 equiv. of $[Me_2Si(NSiMe_3)_2Li_2]$ forms the heterometal amide $[Me_2Si(NSiMe_3)_2]_2InLi$ (**237**) [107]. The structure of **236** consists of a $Li_2In_2Si_2N_4$ core with an adamantane structure that incorporates the bridging $[MeNSiMe_2NMe]^{2-}$ ligands. Each indium atom in **236** is coordintated to the amide end of two $[HNMeSiMe_2NMe]^-$ ligands and also shares two bridging $[MeNSiMe_2NMe]^{2-}$ ligands. Therefore, the In atoms are surrounded by four amide groups in a tetrahedral arrangement with N–In–N angles ranging from 103.9(2) to 111.9(2)°. The amine ends of the $[HNMeSiMe_2NMe]^-$ ligands are coordinated to Li, which also interacts with the bridging $[MeNSiMe_2NMe]^{2-}$ ligands. The average terminal In–N bond distances in **236** are 2.108 Å. The average bridging In–N bond



235



237



236

lengths are about 0.05 longer at 2.202 Å. The crystal structure of **237** shows that the In and Li atoms are bound close together in a tricycle of four-membered rings (In···Li 2.748(9) Å) [107]. The terminal and bridging In–N bond distances in **237** are 2.055(3) and 2.223(3) Å, respectively.

6. Conclusions

This review has described the chemistry of gallium and indium amides reported to date. Much of the work has focused on the synthesis and characterisation of such compounds. The majority of the complexes that have been reported thus far possess a 1:1 (M/N) stiochiometry; however, there are now several examples of 1:2 and 1:3 complexes. In many of the gallium and indium amides described above, the nitrogen coordination is planar; however, this is not indicative of strong π-bonding. For π-bonding, the coordination number at M must be three (or less) so that the required p-orbital is empty and available to form a π-bond. In addition, three coordination is also required at the nitrogen centre. However, even in monomeric derivatives, where the coordination number at M is three, the correct alignment of the p-orbitals on M and N may not be achieved. Furthermore, metal–nitrogen bond lengths are generally in the order monoamide > diamide > triamide, in contrast to what is expected if strong π-bonding existed. This is consistent with a decreasing effective ionic radius with an increasing number of electronegative substituents [2a].

A number of amido complexes of gallium and indium have been shown to act as single-source precursors to metal nitrides, e.g. compounds **2**, **31**, **112** and **187** [1,8,9,26,85]. In addition, these complexes can be used to prepare precursors to a number of other materials, including gallium sulfide and indium oxide. Thus, it is clear that the development of gallium and indium amides will continue to be an area of focus for inorganic chemists.

Acknowledgements

I would like to thank Dr Nicholas Norman (University of Bristol) for useful discussions and suggestions. I am also grateful to the Royal Society for a Dorothy Hodgkin Fellowship and additional financial support.

References

[1] For reviews on Group 13 nitrides see: (a) D.A. Neumayer, J.G. Ekerdt, Chem. Mater. 8 (1996) 9; (b) D.M. Hoffman, Polyhedron 13 (1994) 1169; (c) S. Strite, H. Morkoç, J. Vac. Sci. Technol. B, 10 (1992) 1237.

[2] (a) P.P. Power, Chem. Rev. 99 (1999) 3463 (and references therein);
(b) P.J. Brothers, P.P. Power, Adv. Organomet. Chem. 39 (1996) 1;

(c) I. Haiduc, D.B. Sowerby, The Chemistry of Inorganic Homo- and Heterocycles, Academic Press, London, 1987;
(d) M.F. Lappert, P.P. Power, A.R. Senger, R.C. Srivastava, Metal and Metalloid Amides, Ellis-Horwood, Chichester, 1980.
[3] (a) C.-C. Chang, M.S. Ameerunisha, Coord. Chem. Rev. 189 (1999) 199;
(b) C.B. Lagrone, S.J. Schauer, C.J. Thomas, G.M. Gray, C.L. Watkins, L.K. Krannich, Organometallics 15 (1996) 2458;
(c) S.J. Schauer, G.H. Robinson, J. Coord. Chem. 30 (1993) 197.
[4] (a) M.A. Paver, C.A. Russell, D.S. Wright, Comprehensive Organometallic Chemistry II, vol. 1, 1995, pp. 517–524;
(b) M.J. Taylor, P.J. Brothers, in: A.J. Downs (Ed.), Chemistry of Aluminium, Gallium, Indium and Thallium, Chapman & Hall, London, 1993, pp. 168–181;
(c) Gmelin Handbook of Inorganic Chemistry, 8th ed., Organogallium Compounds, Part 1, Syst. No. 36, Springer, Berlin, 1987;
(d) Gmelin Handbook of Inorganic and Organometallic Chemistry, 8th edn., Organoindium Compounds 1, Springer, Berlin, 1991.
[5] (a) N. Greenwood, E. Ross, A. Storr, J. Chem. Soc. A (1966) 706;
(b) A. Storr, J. Chem. Soc. A (1968) 2065;
(c) A. Storr, A.D. Penland, J. Chem. Soc. A (1971) 1237;
(d) A. Storr, B. Thomas, A.D. Penland, J. Chem. Soc. Dalton Trans. (1972) 326.
[6] (a) W. Harrison, A. Storr, J. Trotter, J. Chem. Soc. Dalton Trans. (1972) 1554;
(b) O.T. Beachley, G.E. Coates, C. Kolnstam, J. Chem. Soc. (1965) 3248.
[7] A. Storr, J. Chem. Soc. A (1968) 2605.
[8] J.P. Campbell, J.-W. Hwang, G. Young Jr., R.B. Von Dreele, C.J. Cramer, W.L. Gladfelter, J. Am. Chem. Soc. 120 (1998) 521 (and references therein).
[9] J.F. Janik, R.L. Wells, Inorg. Chem. 36 (1997) 4135.
[10] (a) P.L. Baxter, A.J Downs, D.W.H. Rankin, H. Robertson, J. Chem. Soc. Dalton Trans. (1985) 807;
(b) J. Lorberth, R. Dorn, W. Massa, S. Wacadlo, Z. Naturforsch. Teil B 48 (1993) 224.
[11] B. Luo, V.G. Young Jr., W.L. Gladfelter, Inorg. Chem. 39 (2000) 1705.
[12] J.F. Janik, R.L. Wells, V.G. Young Jr., A.L. Rheingold, I.A. Guzei, J. Am. Chem. Soc. 120 (1998) 532.
[13] W.R. Nutt, R.E. Stimson, M.F. Leopold, B.H. Rubin, Inorg. Chem. 21 (1982) 1909.
[14] S. Kühner, K.W. Klinkhammer, W. Schwarz, J. Weidlein, Z. Anorg. Allg. Chem. 624 (1998) 1051.
[15] W.R. Nutt, J.A. Anderson, J.D. Odom, M.M. Williamson, R.E. Stimson, B.H. Rubin, Inorg. Chem. 24 (1985) 159.
[16] W.R. Nutt, J.S. Blanton, F.O. Kroh, J.D. Odom, Inorg. Chem. 28 (1989) 2224.
[17] S. Kühner, R. Kuhnle, H.-D. Hausen, J. Weidlein, Z. Anorg. Allg. Chem. 623 (1997) 25.
[18] N.L. Pickett, O. Just, D.G. VanDerveer, W.S. Rees Jr., Acta Crystallogr. Sect. C 56 (2000) 560.
[19] (a) F. Heshmatpour, D. Nußhär, R. Garbe, S. Wocadlo, W. Massa, K. Dehnicke, H. Goesmann, D. Fenske, Z. Anorg. Allg. Chem. 621 (1995) 443;
(b) S. Anfang, J. Grebe, M. Möhlen, B. Neumüller, N. Faza, W. Mossa, J. Magull, K. Dehnicke, Z. Anorg. Allg. Chem. 625 (1999) 1395.
[20] B.-J. Bae, J.E. Park, Y. Kim, J.T. Park, I.-H. Suh, Organometallics 18 (1999) 2513.
[21] J.B. Hill, T.A. Talley, W.T. Pennington, G.H. Robinson, J. Chem. Cryst. 24 (1994) 61.
[22] K. Schmidt, H.-D. Hausen, K.W. Klinkhammer, J. Weidlein, Z. Anorg. Allg. Chem. 625 (1999) 945.
[23] W.R. Nutt, K.J. Murray, J.M. Gulick, J.D. Odom, Y. Ding, L. Lebioda, Organometallics 12 (1996) 1728.
[24] K.M. Waggoner, K. Ruhlandt-Senge, R.J. Wehmschulte, X. He, M.M. Olmstead, P.P. Power, Inorg. Chem. 32 (1993) 2557.
[25] W.-P. Leung, C.M.Y. Chan, B.-M. Wu, T.C.W. Mak, Organometallics 15 (1996) 519.
[26] S.T. Barry, D.S. Richeson, Chem. Mater. 6 (1994) 2220.
[27] D.A. Atwood, A.H. Cowley, R.A. Jones, M.A. Mardones, J.L. Atwood, S.G. Bott, J. Coord. Chem. 26 (1992) 285.

[28] G. Linti, R. Frey, Z. Anorg. Allg. Chem. 623 (1997) 531.
[29] G.E. Herberich, U. Englert, D. Posselt, J. Organomet. Chem. 461 (1993) 21.
[30] G. Linti, R. Frey, K. Polborn, Chem. Ber. 127 (1994) 1387.
[31] P.J. Brothers, R.J. Wehmschulte, M.M. Olmstead, K. Ruhlandt-Senge, S.R. Parkin, P.P. Power, Organometallics 13 (1994) 2792.
[32] G. Linti, J. Organomet. Chem. 465 (1994) 79.
[33] M.R. Kopp, T. Kräuter, A. Dashti-Mommertz, B. Neumüller, Z. Naturforsch. Teil B 54 (1999) 627.
[34] (a) S.J. Schauer, C.H. Lake, C.L. Watkins, L.K. Krannich, D.H. Powell, J. Organomet. Chem. 549 (1997) 31;
(b) S.J. Schauer, C.H. Lake, C.L. Watkins, L.K. Krannich, Organometallics 15 (1996) 564.
[35] (a) D.A. Atwood, R.A. Jones, A.H. Cowley, S.G. Bott, J.L. Atwood, J. Organomet. Chem. 434 (1992) 143;
(b) D.A. Atwood, V.O. Atwood, D.F. Carriker, A.H. Cowley, F.P. Gabbaï, R.A. Jones, M.R. Bond, C.J. Carrano, J. Organomet. Chem. 463 (1993) 29;
(c) D.A. Atwood, R.A. Jones, A.H. Cowley, S.G. Bott, J.L. Atwood, Polyhedron 10 (1991) 1897.
[36] D.C. Bradley, H.M. Dawes, M.B. Hursthouse, L.M. Smith, M. Thornton-Pett, Polyhedron 9 (1990) 343.
[37] S.T. Barry, D.S. Richeson, J. Organomet. Chem. 510 (1996) 103.
[38] B. Neümuller, Z. Naturforsch. Teil B 51 (1996) 637.
[39] (a) G.E. Coates, J. Chem. Soc. (1951) 2003;
(b) G.E. Coates, J. Graham, J. Chem. Soc. (1963) 233.
[40] (a) K.M. Waggoner, P.P. Power, J. Am. Chem. Soc. 113 (1991) 3385;
(b) M. Niemeyer, T.J. Goodwin, S.H. Risbud, P.P. Power, Chem. Mater. 8 (1996) 2745.
[41] B. Lee, W.T. Pennington, G.H. Robinson, Inorg. Chim. Acta 190 (1991) 173.
[42] J.T. Park, Y. Kim, J. Kim, K. Kim, Y. Kim, Organometallics 11 (1992) 3321.
[43] H. Schumann, O. Just, S. Nickel, R. Weimann, V. Gottschalch, B.P. Keller, R. Schwabe, Adv. Mater. 6 (1994) 768.
[44] (a) O.T. Beachley, M.J. Noble, M. Rowen Churchill, C.H. Lake, Organometallics 11 (1992) 1051;
(b) O.T. Beachley, M.J. Noble, M. Rowen Churchill, C.H. Lake, Organometallics 17 (1998) 3311;
(c) O.T. Beachley, M.J. Noble, M. Rowen Churchill, C.H. Lake, Organometallics 17 (1998) 5153.
[45] (a) W.R. Nutt, K.J. Murray, J.M. Gulick, J.D. Odom, Y. Ding, L. Lebioda, Organometallics 15 (1996) 3653;
(b) J.J. Byers, B. Lee, W.T. Pennington, G.H. Robinson, Polyhedron 11 (1992) 967.
[46] (a) B. Sen, G.L. White, J. Inorg. Nucl. Chem. 35 (1973) 2207;
(b) A. Storr, B.S. Thomas, J. Chem. Soc. A (1971) 3850.
[47] O.T. Beachley, C. Beuno, M.R. Churchill, R.B. Hallock, R.G. Simmons, Inorg. Chem. 20 (1981) 2423.
[48] F. Zettler, H. Hess, Chem. Ber. 110 (1977) 3943.
[49] (a) T. Belgradt, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, Angew. Chem. Int. Ed. Engl. 32 (1993) 1056;
(b) T. Belgradt, S.D. Weazsada, H.W. Roesky, H. Gornitzka, L. Häming, D. Stalke, Inorg. Chem. 33 (1994) 6247.
[50] D.A. Atwood, A.H. Cowley, P.R. Harris, R.A. Jones, S.U. Koschmieder, C.M. Nunn, J.L. Atwood, S.G. Bott, Organometallics 12 (1993) 24.
[51] M.J. Almond, M.G.B. Drew, C.E. Jenkins, D.A. Rice, J. Chem. Soc. Dalton Trans. (1992) 5.
[52] S. Amirkhalili, P.B. Hitchcock, J.D. Smith, J. Chem. Soc. Dalton Trans. (1979) 1206.
[53] Y. Zhou, D.S. Richeson, Organometallics 14 (1995) 3558.
[54] (a) O.T. Beachley, D.B. Rosenblum, M. Rowen Churchill, C.H. Lake, L.M. Tooney, Organometallics 15 (1996) 3553;
(b) O.T. Beachley, T.L. Royster, J.R. Arhar, A.L. Rheingold, Organometallics 12 (1993) 1976.
[55] P. Jutzi, B. Neumann, G. Reumann, H.-G. Stammler, Organometallics 18 (1999) 2037.
[56] D.W. Peters, M.P. Power, E.D. Bourret, J. Arnold, J. Chem. Soc. Chem. Commun. (1998) 753.

[57] D.A. Neumayer, A.H. Cowley, A. Decken, R.A. Jones, V. Lakhotia, J.G. Ekerdt, Inorg. Chem. 34 (1995) 4698.
[58] D.W. Peters, E.D. Bourret, M.P. Power, J. Arnold, J. Organomet. Chem. 582 (1999) 108.
[59] B. Luo, W.L. Gladfelter, J. Chem. Soc. Chem. Commun. (2000) 825.
[60] Y. Kim, J.H. Kim, J.E. Park, H. Song, J.T. Park, J. Organomet. Chem. 545–546 (1997) 99.
[61] (a) G.E. Coates, R.A. Whitcombe, J. Chem. Soc. (1956) 3351;
(b) K. Mertz, W. Schwarz, B. Erberwein, J. Weidlein, H. Hess, H.D. Hausen, Z. Anorg. Allg. Chem. 429 (1977) 99.
[62] A.M. Arif, D.C. Bradley, H. Dawes, D.M. Frigo, M.B. Hursthouse, B. Hussain, J. Chem. Soc. Dalton Trans. (1987) 2159.
[63] K. Schmid, S. Kuhner, H.-D. Hausen, J. Weidlein, Z. Anorg. Allg. Chem. 623 (1997) 1499.
[64] C. Schnitter, S.D. Waezsada, H.W. Roesky, M. Teichert, I. Uson, E. Parisini, Organometallics 16 (1997) 1197.
[65] Th. Grabowy, K. Merzweiler, Z. Anorg. Allg. Chem. 626 (2000) 736.
[66] K.A. Aitchison, J.D. Julius Backer-Dirks, D.C. Bradley, M.M. Faktor, D.M. Frigo, M.B. Hursthouse, B. Hussain, R.L. Short, J. Organomet. Chem. 366 (1989) 11.
[67] M. Trapp, H.D. Hausen, G. Weckler, J. Weidlein, J. Organomet. Chem. 450 (1993) 53.
[68] M. Porchia, F. Benetollo, N. Brianese, G. Rossetto, P. Zanella, J. Organomet. Chem. 424 (1992) 1.
[69] (a) B. Neumüller, Z. Naturforsch. Teil B 46 (1991) 753;
(b) B. Neumüller, Z. Naturforsch. Teil B 45 (1990) 1559;
(c) B. Neumüller, Chem. Ber. 122 (1989) 2283.
[70] K.M. Simpson, R.W. Gedridge, K.T. Higa, J. Organomet. Chem. 456 (1993) 31.
[71] M.A. Petri, K. Ruhlandt-Senge, H. Hope, P.P. Power, Bull. Soc. Chim. Fr. 130 (1993) 851.
[72] D.C. Bradley, D.M. Frigo, M.B. Hursthouse, B. Hussain, Organometallics 7 (1988) 1112.
[73] Th. Grabowy, K. Merweiler, Z. Anorg. Allg. Chem. 625 (1999) 2045.
[74] M.R. Kopp, B. Neumüller, Z. Anorg. Allg. Chem. 625 (1999) 1246.
[75] H.-D. Hausen, K. Locke, J. Weidlein, J. Organomet. Chem. 423 (1992) C1.
[76] J. Tödtmann, W. Schwarz, J. Weidlein, A. Haaland, Z. Naturforsch. Teil B 48 (1993) 1437.
[77] H.-D. Hausen, K. Locke, J. Weidlein, J. Organomet. Chem. 429 (1992) C27.
[78] M. Veith, S. Hill, V. Huch, Eur. J. Inorg. Chem. (1999) 1343.
[79] J. Prust, P. Müller, C. Rennekamp, H.W. Roesky, I. Usón, J. Chem. Soc. Dalton Trans. (1999) 2265.
[80] R. Hillwig, K. Harms, K. Dehnicke, J. Organomet. Chem. 501 (1995) 327.
[81] D.L. Freeman, J.D. Odom, W.R. Nutt, L. Lebioda, Inorg. Chem. 36 (1997) 2718.
[82] H.W. Roesky, U. Seseke, M. Noltemeyer, G.M. Sheldrick, Z. Naturforsch. Teil B 43 (1998) 1130.
[83] R. Frey, G. Linti, K. Polborn, Chem. Ber. 127 (1994) 101.
[84] G. Linti, R. Frey, W. Kostler, H. Schwenk, Chem. Ber. 130 (1997) 663.
[85] D.A. Neumayer, A.H. Cowley, A. Decken, R.A. Jones, V. Lakohotia, J.G. Ekerdt, J. Am. Chem. Soc. 117 (1995) 5893.
[86] G. Linti, R. Frey, M. Schmidt, Z. Naturforsch. Teil B 49 (1994) 958.
[87] G. Linti, M. Bühler, H. Urban, Z. Anorg. Allg. Chem. 624 (1998) 517.
[88] C.J. Carmalt, A.H. Cowley, R.D. Culp, R.A. Jones, J. Chem. Soc. Chem. Commun. (1996) 1453.
[89] G. Linti, H. Noth, K. Polborn, C. Robl, M. Schmidt, Chem. Ber. 128 (1995) 487.
[90] J.L. Atwood, S.G. Bott, C. Jones, C.L. Raston, Inorg. Chem. 30 (1991) 4868.
[91] H.-D. Hausen, R. Kuhnle, J. Weidlein, Z. Naturforsch. Teil B 50 (1995) 1419.
[92] D.A. Atwood, A.H. Cowley, R.A. Jones, Organometallics 12 (1993) 236.
[93] R. Frey, V.D. Gupta, G. Linti, Z. Anorg. Allg. Chem. 622 (1996) 1060.
[94] A.M. Arif, D.C. Bradley, D.M. Frigo, M.B. Hursthouse, B. Hussain, J. Chem. Soc. Chem. Commun. (1985) 783.
[95] J. Kim, S.G. Bott, D.M. Hoffman, J. Chem. Soc. Dalton Trans. (1999) 1731.
[96] M. Veith, H. Lange, O. Recktenwald, W. Frank, J. Oragnomet. Chem. 294 (1985) 273.
[97] D.A. Atwood, V.O. Atwood, A.H. Cowley, R.A. Jones, J.L. Atwood, S.G. Bott, Inorg. Chem. 33 (1994) 3251.

[98] K.M. Waggoner, M.M. Olmstead, P.P. Power, Polyhedron 9 (1990) 257 (and references therein).
[99] R. Guarino, J. Rouxel, Bull. Soc. Chim. Fr. (1969) 2284.
[100] S. Suh, J.H. Hardesty, T.A. Albright, D.M. Hoffman, Inorg. Chem. 38 (1999) 1627.
[101] J.S. Silverman, C.J. Carmalt, A.H. Cowley, R.D. Culp, R.A. Jones, B.G. McBurnett, Inorg. Chem. 38 (1999) 296.
[102] H. Bürger, J. Cichon, U. Goetze, U. Wannagat, H.J. Wismar, J. Organomet. Chem. 33 (1971) 1.
[103] (a) G. Rossetto, N. Brianese, A. Camporese, M. Porchia, P. Zanella, R. Bertoncello, Main Group Met. Chem. 14 (1991) 113;
(b) A. Purdy, Inorg. Chem. 33 (1994) 282.
[104] J. Kim, S.G. Bott, D.M. Hoffman, Inorg. Chem. 37 (1998) 3835.
[105] L.A. Mîinea, S. Sugh, D.M. Hoffman, Inorg. Chem. 38 (1999) 4441.
[106] M.R. Kopp, B. Neumüller, Z. Anorg. Allg. Chem. 624 (1998) 361.
[107] M. Veith, M. Zimmer, S. Müller-Becker, Angew. Chem. Int. Ed. Engl. (1993) 1731.