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Synthesis and characterisation of dialkyl[2-(2-phenolato)oxazolines] of gallium(III) and indium(III): crystal structure of [{$InMe_2(OC_6H_4$-$OxMe_2)$}$_2$]

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Reactions of trialkylgallium/indium etherate with 2-(2-hydroxyphenyl)oxazolines afforded colourless dialkyl[2-(2-phenolato)oxazoline]gallium/indium complexes of the type [$GaR_2(OC_6H_4$-OxR'R'')] (**1**) and [{$InMe_2(OC_6H_4$-OxR'R'')}$_2$] (**2**) (R = Me or Et; Ox = oxazoline, R' = Me or Et; R'' = Me or H). These complexes were characterised by elemental analysis, IR, mass and NMR (^1H and ^{13}C) spectral data. The complex [{$InMe_2(OC_6H_4$-$OxMe_2)$}$_2$] has a dimeric structure as established by X-ray diffraction. The indium atom acquires an irregular trigonal bipyramidal geometry defined by C_2O_2N ligating atoms.

Keywords: gallium, indium, 2-(2-hydroxyphenyl)oxazolines, complexes, X-ray structure

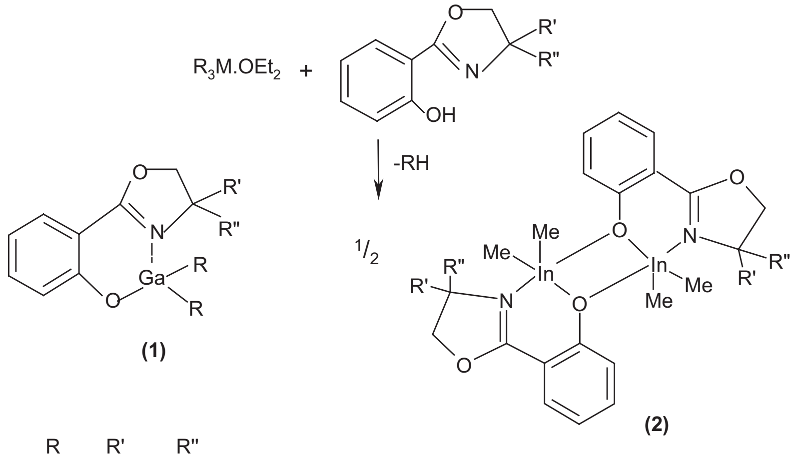
The chemistry of organo-gallium and -indium compounds with alkoxo ligands has been an active area of research for sometime.[1,2] More recently diorganometal-complexes derived from internally functionalised alkoxo ligands (*e.g.*, [$InMe_2${$OC(CF_3)CH_2NHMe$}$_2$) have shown promising potential to serve as precursors for the preparation of Ga_2O_3 and In_2O_3 films via the CVD process[3-5] and also reagents in cross coupling reactions in organic synthesis.[6-8]

Oxazolines represent yet another interesting family of internally functionalised ligands.[8,9] The oxazoline skeleton has an ability to form kinetically inert chiral metal complexes, which have promising potential in asymmetric organic synthesis and in fact several of such derivatives have been successfully used as chiral catalysts.[10-12] In view of the above and in pursuance of our work on gallium and indium complexes, we have synthesised and characterised diorganogallium/indium complexes with oxazolines.

Results and discussion

Metathetical reactions between triorgano-gallium/-indium ether adduct and 2-(2-hydroxyphenyl)oxazolines lead to the formation of diorganometal-derivatives (**1**) and (**2**) in nearly quantitatively yield with elimination of alkane (Scheme 1). These complexes are colourless solids/liquids. Solids can either be recrystallised or sublimed under vacuum. The C=N stretching vibrations in the IR spectra of these complexes appeared at lower wave numbers (10–20 cm^{-1}) than the corresponding absorptions for the free ligand, suggesting the coordination of oxazoline nitrogen to the metal atom. Absorptions in the region 517–584 cm^{-1}, absent in the spectra of free ligands, can be assigned to metal-carbon stretchings. The ν Ga–C and ν In–C absorptions in several diorganometal-complexes have been reported[13–15] in the region 500–600 cm^{-1}.

The mass spectra of some representative compounds have been recorded and the resulting data are summarised in Table 1. The gallium and indium containing species are readily identified from the characteristic isotopic pairs (^{69}Ga + ^{71}Ga/^{113}In + ^{115}In). The most prominent peaks in the spectra can be attributed to (M–R) (R = Et or Me) species. The indium compounds, in addition to molecular ion peaks, also displayed peaks due to (M_2–L), while for [{$InMe_2(OC_6H_4OxMe)$}$_2$], a peak at *m/e* 627 assignable to (M_2–Me) was observed, suggesting their dimeric nature. However, for



R	R'	R''	
Me	Me	Me	**(1a)**
Et	Me	Me	**(1b)**
Me	Me	H	**(1c)**
Et	Me	H	**(1d)**
Me	Et	H	**(1e)**
Et	Et	H	**(1f)**

R'	R''	
Me	Me	**(2a)**
Me	H	**(2b)**
Et	H	**(2c)**

Scheme 1

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Table 1 Mass spectral data of diorgano-gallium and -indium compounds of 2-(2-hydroxyphenyl)oxazolines

Compound	*m/e* (species)
$[GaMe_2(OC_6H_4OxMe_2)]$ (**1a**)	289/291 M^+ 274/276 M – Me 192 (small no gallium); 190 free ligand
$[GaEt_2(OC_6H_4OxMe_2)]$ (**1b**)	288/290 (M – Et) 192 (small peak no gallium); 190 free ligand 121 (no gallium) (ligand fragment)
$[GaMe_2(OC_6H_4OxMe)]$ (**1c**)	260/262 (M – Me) 178 (no gallium peak); 176 free ligand
$[\{InMe_2(OC_6H_4OxMe_2)\}_2]$ (**2a**)	480 (M_2 – L) 336 (M) (335 M) 320 (M – Me) 257 193 192 (190 free ligand) 145 (Me_2In) 130 (MeIn) 115 (In)
$[\{InMe_2(OC_6H_4OxMe)\}_2]$ (**2b**)	627 (M_2 – Me) 466 (M_2 – L) 408 322 (M) 321 (M) 306 (M – Me) 192 179 178 (free ligand 176) 145 (Me_2In) 115 (In)
$[\{InMe_2(OC_6H_4OxEt)\}_2]$ (**2c**)	478 (M + Me_2In = 480) or (M_2 – L) 336 (M) (M = 335) 320 (M – Me) 193 192 (190 free ligand) 178 145 (Me_2In) 115 (In)

gallium complexes, no peak greater than molecular ion peak was observed, indicating their monomeric nature. Except for $[GaMe_2(OC_6H_4OxMe_2)]$, which showed a low intensity molecular ion peak, the parent ion peak was absent in the spectra of other derivatives.

The nature of M, R and L in organo-gallium and –indium compounds greatly influences the nuclearity of the resulting derivatives. For example, $[GaR_2(acac)]$ (R = Me or Et) are monomeric with four coordinate gallium atoms,[16] whereas $[Me_2In(acac)]_2$ is dimeric with five coordinate indium.[17] Oxazolines employed in the present work function as six-membered O/N chelating ligands and can be compared with acac. Thus the inference from the mass spectra, that the gallium complexes are monomeric while those of indium are dimeric, is in conformity with the structures reported for diorganometal acetylacetonates.[16,17] The ^1H and $^{13}C\{^1H\}$ NMR spectra (Table 2) exhibited characteristic peaks attributable to oxazoline ligands and the alkyl groups attached to the metal. The H-3 (~6.8 ppm) and H-4 (~6.6 ppm) proton resonances of the phenyl ring are shielded on complexation from their positions for the corresponding free ligands, whereas H-5 (~7.3 ppm) and H-6 (~7.6 ppm) are little affected. The oxazoline protons of achiral ligands showed singlets for methyl and methylene protons, which were slightly deshielded in gallium and indium complexes. The oxazoline proton resonances for chiral ligands appeared as two sets of resonances (see later), however, their ^{13}C NMR spectra showed only singlets for each carbon of the oxazoline fragment. The alkyl-metal ^1H and ^{13}C signals appeared in the region expected for diorganometal-complexes containing alkoxo ligands.[18,19] The diorganogallium complexes with chiral ligands displayed very closely spaced ^1H as well as ^{13}C resonances for the R_2Ga group suggesting their diastereotropic nature. However, the dimethyl indium complexes, which have a penta-coordinated indium atom, exhibited only one set of signals. Phenolic ring carbon resonances showed pronounced shift on complexation. The signal at ~116.5 ppm in the free ligand is shielded by 1.0 ppm, whereas the remaining five signals are deshielded (1.4 to 8.4 ppm), C-1 and C-2 being highly deshielded. The oxazoline ring carbon resonances are, however, little influenced by complexation.

Structure of $[\{Me_2In(OC_6H_4\text{-}OxMe_2)\}_2]$ (**2a**)

The molecular structure of $[\{InMe_2(OC_6H_4OxMe_2)\}_2]$ (**2a**) with crystallographic numbering scheme is shown in Fig. 1 and selected bond lengths and angles are given in Table 3. The molecule consists of an oxygen–bridged dimeric unit containing five coordinate indium atoms in an irregular trigonal bipyramidal environment defined by the C_2O_2N core. The molecule lies on crystallographic centre of symmetry with a planar four-membered In_2O_2 ring. The phenolate oxygen atoms bridge two indium atoms in an asymmetric manner with In-O distances of 2.135 (5) and 2.607 (5) Å. These distances can be compared with $[\{InMe_2(acac)\}_2]$.[17] However, two In–O distances in $[\{InBu^t{}_2(OEt)\}_2]$[20] and $[\{InPh_2(OSiMe_3)\}_2]$[21] are essentially identical (2.156 and 2.154 Å, respectively). The In-C distances are in good agreement with those reported earlier.[17,22] The In–N distance (2.311(6) Å) can

Table 2 ^1H and $^{13}C\{^1H\}$ NMR data for 2-(2-hydroxyphenyl)oxazolines and their diorgano-gallium and –indium complexes in $CDCl_3$

Compound	^1H NMR data δ in ppm	$^{13}C\{^1H\}$ NMR data δ in ppm
[2-HOC_6H_4-C_3H_2ON-Me_2-4,4'] (HOC_6H_4-$OxMe_2$)	1.39 (s, Me_2); 4.09 (s, CH_2, Ox); 6.86 (dt 7 Hz (t); 1 Hz (d); 7.0 (d, d; 7, 1 Hz); 7.36 (dt; 7 Hz (t), 1.6 Hz (d); 7.64 (d, d; 7, 1.5 Hz), 12.05 (br, OH)	28.3 (s, Me_2); 67.0 (s, CH_2); 78.2 ($Me_2\mathbf{C}$); 110.9 (s, C=N); Ph: 116.5, 118.4; 127.8; 133.0; 159.9 (C–CPh); 163.5 (C-O).
[HOC_6H_4-C_3H_3ON-Me-4] (HOC_6H_4-OxMe)	1.37 (d, 6.3 Hz, Me); 3.96 (t, 6.3 Hz, CH); 4.39 – 4.57 (m, OCH_2); 6.86 (t, 7.6 Hz); 7.02 (d, 8.2 Hz); 7.36 (t, 7.2 Hz); 7.63 (d, 7.8 Hz); 12.2 (br, OH).	21.4 (s, Me); 61.0 (s, OCH_2); 73.3 (s, N**C**HMe); 110.9 (s, C=N); Ph: 116.8; 118.6; 128.0; 133.2; 160.1 (C–CPh); 165.1 (C-O)
[HOC_6H_4-C_3H_3ON-Et-4] (HOC_6H_4-OxEt)	1.02 (t, 7.5 Hz; $CH_2\mathbf{CH_3}$); 1.67 (m, $\mathbf{CH_2}CH_3$); 4.03 (t, 7.5 Hz, CH); 4.26-4.33 (m); 4.47 (t, 8.2 Hz) (CH_2); 6.86 (t, 7.6 Hz); 7.01 (d, 7.3 Hz); 7.37 (t, 7 Hz), 7.64 (d, 7.7 Hz), 12.24 (br, OH)	9.8 (s, $CH_2\mathbf{CH_3}$); 28.6 (s, CH_2); 66.7 (s, OCH_2), 71.3 (s, N**C**HEt); 110.7 (C=N); 116.5; 118.3; 127.9; 133.1; 159.9; 164.9.
[$GaMe_2(OC_6H_4OxMe_2)$] (**1a**)	–0.26 (s, Me_2Ga); 1.46 (s, Me_2); 4.22 (s, CH_2, Ox); 6.63 (t, 7 Hz); 6.85 (d, d, 8, 0.6 Hz); 7.35 (t, d; 7, 1.5 Hz); 7.63 (d, d; 8, 1.7 Hz).	–5.6 (s, Me_2Ga); 27.6 (s, $\mathbf{Me_2}$); 66.3 (s, CH_2); 78.8 (s, $Me_2\mathbf{C}$); 109.3 (s, C=N); 115.5; 122.6; 129.5; 135.9; 167.4; 167.7.
[$GaEt_2(OC_6H_4OxMe_2)$] (**1b**)	0.40 (m, $GaCH_2$); 1.08 (t, 8 Hz, $GaCH_2\mathbf{Me}$); 1.46 (s, Me_2); 4.22 (s, CH_2); 6.60 (t, 7 Hz); 6.88 (d, 8 Hz); 7.33 (t, 7 Hz); 7. 62 (d, 8.0 Hz).	4.6 (s, CH_2Ga); 9.4 (s, $GaCH_2\mathbf{CH_3}$); 27.4 (s, $\mathbf{Me_2}$); 66.2 (s, CH_2); 78.8 ($Me_2\mathbf{C}$); 109.3 (C=N); 115.2; 122.5; 129.5; 135.8; 167.7; 168.5
[$GaMe_2(OC_6H_4OxMe)$] (**1c**)	–0.29; –0.28 (s, Me_2Ga); 1.41 (d, 6.5 Hz) (Me); 4.08 (t, 8.4 Hz, CH), 4.36-4.44 (m); 4.67 (t, 7 Hz) (OCH_2); 6.63 (td, 8 Hz (t); 1 Hz (d); 6.86 (dd, 8, 0.7 Hz); 7.35 (t, d; 7.0 Hz (t) 1.6 Hz (d); 7.61 (d, d, 8, 1.7 Hz)	–7.7, –5.6 (each s, Me_2Ga); 20.3 (s); 58.6, 73.6; 109.0 (C=N); 115.5; 122.6; 129.5; 135.9; 167.6; 168.3.
[$GaEt_2(OC_6H_4OxMe)$] (**1d**)	0.35–0.49 (m, $GaCH_2$); 1.05, 1.08 (each t, 8.0 Hz); 1.42 (d, 6 Hz **Me**); 4.06 (t, 8.4 Hz, CH); 4.34–4.42 (m); 4.65 (t, 7 Hz) (OCH_2); 6.60 (t, 8 Hz); 6.86 (d, 8 Hz); 7.32 (t); 7.60 (d, 8 Hz).	2.9, 4.3 (each s, $GaCH_2$); 9.4, 9.6 (each s, $GaCH_2\mathbf{CH_3}$); 20.2 (s), 58.9, 73.5; 109.0 (C=N); 115.2; 122.5; 129.4; 135.9; 168.4; 168.8.
[$GaMe_2(OC_6H_4OxEt)$] (**1e**)	–0.29, –0.28 (each, s, Me_2Ga); 0.97 (t 7.5 Hz, $CH_2\mathbf{CH_3}$); 1.62-1.69 (m); 1.84-1.92 (m) ($\mathbf{CH_2}CH_3$); 4.22 (t, 7.7 Hz CH); 4.26–4.33 (m); 4.61 (t, 8 Hz CH_2); 6.63 (td, 7 Hz (t), 1 Hz (d); 6.86 (dd, 8, 0.6 Hz); 7.35 (td, 8 Hz (t) 1.9 (d)); 7.60 (dd, 8, 1.7 Hz).	–7.7, –5.9 (each s, Me_2Ga), 8.9; 27.0; 64.2; 71.3; 109.0; 115.5; 122.6; 129.5; 135.9; 167.7; 168.5.
[$GaEt_2(OC_6H_4OxEt)$] (**1f**)	0.34–0.50 (m, $GaCH_2$); 0.97 (t, 7.5 Hz $CH_2\mathbf{CH_3}$); 1.06, 1.10 (each t, 8 Hz, $GaCH_2\mathbf{Me}$), 1.59–1.68 (m), 1.84-1.93 (m), ($\mathbf{CH_2}CH_3$), 4.18 (t, 8 Hz CH); 4.23–4.29 (m), 4.58 (t, 7.7 Hz CH_2O); 6.60 (td, 7.5, 0.9 Hz), 6.88 (d, 8 Hz); 7.33 (t, 7.5 Hz); 7.60 (d, d, 7.6, 1.2 Hz).	2.9, 4.6 (each s, Ga$\mathbf{CH_2}$); 9.4, 9.6 (each s $GaCH_2\mathbf{Me}$), 9.1 (s) 27.1 (ethyl); 64.5; 71.2; 109.0; 115.1; 122.3; 129.4; 135.7; 168.3; 168.7.
[$\{InMe_2(OC_6H_4OxMe_2)\}_2$] (**2a**)	–0.07 (s, Me_2In); 1.42 (s, Me_2); 4.15 (s, CH_2, Ox); 6.56 (t, 7 Hz); 6.82 (d, 8 Hz); 7.30 (t, 7 Hz); 7.66 (d, 8 Hz).	–5.5 (s, Me_2In); 28.1 (s, Me_2); 66.6 (s, CH_2); 77.8 (s, $Me_2\mathbf{C}$); 110.3 (s, C=N); 114.6 (s); 123.4; 130.3; 135.1; 167.2; 169.5.
[$\{InMe_2(OC_6H_4OxMe)\}_2$] (**2b**)	–0.10 (s, Me_2In); 1.37 (d, 4.7 Hz, Me); 3.98 (t, 8 Hz, CH); 4.37 (br), 4.55 (t, 8 Hz) (OCH_2); 6.57 (unresolved t); 6.84 (d, 7 Hz); 7.29 (t, 7 Hz); 7.65 (d, 6.2 Hz).	–6.2 (s, Me_2In); 21.0 (s, Me); 59.8 (s, OCH_2); 72.7 (s, NCH–); 110.2 (C=N); 114.6; 123.2; 130.3; 135.0; 168.5; 169.5.
[$\{InMe_2(OC_6H_4OxEt)\}_2$] (**2c**)	–0.09 (s, Me_2In); 0.96 (t, 7.5 Hz, $CH_2\mathbf{Me}$); 1.61 (m); 1.70 (br) ($\mathbf{CH_2}Me$); 4.12 (t, 7.5 Hz, CH); 4.26 (br); 4.48 (br)(CH_2); 6.57 (br); 6.83 (d, 7 Hz); 7.29 (t, 7 Hz); 7.64 (d, 7.5 Hz).	–6.2 (s, Me_2In); 9.1; 27.7; 62.4; 70.4; 110.2; 114.5; 123.1; 130.3; 134.9; 168.3; 169.5

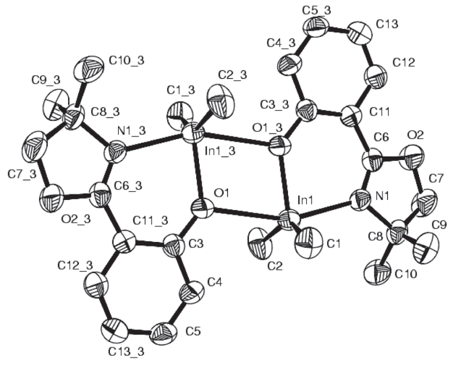

Fig. 1 ORTEP drawing of [$\{InMe_2(OC_6H_4$-$OxMe_2)\}_2$] with atomic number scheme.

be compared with [$\{InMe_2(NHBu^t)\}_2$] (2.23 Å)[17] and [$\{InMe_2(NHNHPh)\}_2$] (2.23 Å).[22] The O-In-O angle is within the range (74–79°) reported for dimeric diorgano-aluminium, -gallium and -indium alkoxides.[21,23,24] The six-membered chelate ring is slightly puckered, while the oxazolinate ligand is almost planar.

Experimental

Materials and physical measurements

All experiments involving organo-gallium/-indium compounds were carried out in anhydrous conditions under a dinitrogen atmosphere using Schlenk techniques. Solvents were dried by standard procedures. [$InMe_3(OEt_2)$] was prepared from Me MgI and anhydrous indium trichloride in diethyl ether[25] while [$GaR_3(OEt_2)$] (R = Me or Et) was synthesised from gallium magnesium alloy and alkyl iodide in diethyl ether.[26] Ether contents in each preparation were evaluated

Table 3 Selected bond lengths (Å) and angles (°) for [{InMe$_2$(OC$_6$H$_4$OxMe$_2$)}$_2$] (2a)

In1–C1	2.144 (8)	O1-C3	1.340 (6)
In1–C2	2.142 (7)	O2-C6	1.360 (6)
In1–O1	2.135 (5)	O2-C7	1.451 (10)
In1–O1_3	2.607 (5)	N1-C6	1.281 (7)
In1–N1	2.311 (6)	N1-C8	1.495 (7)
C7–C8	1.529 (11)	C6-C11	1.454 (9)
C1–In1–C2	142.0 (4)	C2-In1-N1	98.5 (2)
C1–In1–N1	100.3 (2)	C2-In1-O1	106.0 (3)
C1–In1–O1	108.9 (3)	C2-In1-O1_3	87.48 (27)
C1–In1–O1_3	86.88 (27)	O1-In1-N1	82.29 (19)
N1–In1–O1_3	158.40 (18)	O1-In1-O1_3	76.1 (2)
In1–O1–In1_3	103.89 (19)		

Table 4 Analytical data for diorgano-gallium and -indium complexes

Compound	Yield/%	M.p/°C	% Analysis found (Calc)				IR/cm^{-1}	
			C	H	N	Ga/In	C=N	M-C
[GaMe$_2$(OC$_6$H$_4$OxMe$_2$)] (**1a**)	81	75	53.9 (53.8)	6.2 (6.3)	5.2 (4.8)	23.8 (24.0)	1619	537, 567
[GaEt$_2$(OC$_6$H$_4$OxMe$_2$)] (**1b**)	92	Liquid	–	–	–	22.4 (21.9)	1619	537, 562
[GaMe$_2$(OC$_6$H$_4$OxMe)] (**1c**)	75	65	52.1 (52.2)	5.8 (5.8)	5.3 (5.1)	25.6 (25.3)	1622	541, 584
[GaEt$_2$(OC$_6$H$_4$OxMe)] (**1d**)	95	Liquid	–	–	–	22.9 (22.9)	1631	517, 563
[GaMe$_2$(OC$_6$H$_4$OxEt)] (**1e**)	92	88	53.6 (53.8)	6.2 (6.3)	5.0 (4.8)	23.6 (24.0)	1613	538, 584
[GaEt$_2$(OC$_6$H$_4$OxEt)] (**1f**)	95	Liquid	–	–	–	21.6 (21.9)	1619	573, 559
[{InMe$_2$(OC$_6$H$_4$OxMe$_2$)}$_2$] (**2a**)	96	170	46.6 (46.6)	5.1 (5.4)	4.4 (4.2)	34.2 (34.3)	1628	529
[{InMe$_2$(OC$_6$H$_4$OxMe)}$_2$] (**2b**)	96	155	43.9 (44.9)	4.7 (5.0)	4.5 (4.4)	35.6 (35.8)	1637	529
[{InMe$_2$(OC$_6$H$_4$OxEt)}$_2$] (**2c**)	89	150	45.9 (46.6)	5.1 (5.4)	4.5 (4.2)	34.7 (34.3)	1628	526

by ^{1}H NMR integration. The 2-(2-hydroxyphenyl)oxazolines were prepared according to literature methods[27] and distilled under vacuum prior to use. Infrared spectra were recorded as neat liquids or as Nujol mulls between CsI plates on a Bomem MB-102 FT IR spectrometer. The NMR spectra (^{1}H, and ^{13}C{^{1}H}) were recorded on a Bruker DPX-300 NMR spectrometer in 5 mm tube in CDCl$_3$ solution. Chemical shifts were referenced to the internal chloroform peak (δ 7.26 and δ 77.0 ppm) for ^{1}H and ^{13}C{^{1}H}, respectively. Mass spectra were recorded on a Waters Q-TOF micro (YA-105) time of flight mass spectrometer.

Syntheses

[GaMe$_2$(OC$_6$H$_4$-OxMe$_2$)] (**1a**): To a benzene solution (20 cm^3) of trimethyl gallium etherate (1.032 g, containing 426 mg, 3.7 mmol of GaMe$_3$) was added a solution of 4, 4-dimethyl 2-(2-hydroxyphenyl)oxazoline (710 mg, 3.7 mmol) in the same solvent. The reaction mixture was stirred for 1 h. The solvent was evaporated under reduced pressure leaving behind a white solid which was recrystallised from hexane (yield: 81%, 872 mg). This can be sublimed under vacuum at 180°C in a poor yield (14%). Similarly all other dimethyl gallium derivatives were prepared.

[GaEt$_2$(OC$_6$H$_4$-OxEt)] (**1f**): To a benzene solution (20 cm^3) of triethyl gallium etherate (530 mg containing 391 mg, 2.5 mmol of GaEt$_3$) was added a solution of 4-ethyl 2-(2-hydroxyphenyl)oxazoline (477 mg, 2.5 mmol). After stirring the reaction mixture for 1 h, the solvent was removed under reduced pressure to give a colourless liquid (yield: 95%, 755 mg). Similarly all other diethyl gallium derivatives were prepared.

[{InMe$_2$(OC$_6$H$_4$-OxMe)}$_2$] (**2b**): To a benzene solution (20 cm^3) of trimethyl indium etherate (1.612 g containing 363 mg, 2.27 mmol of InMe$_3$) was added a benzene solution of 4-methyl 2-(2-hydroxyphenyl)oxazoline (403 mg, 2.27 mmol). After 1 h of stirring at room temperature, the solvent was evaporated under reduced pressure leaving behind a white solid which was washed with hexane and dried *in vacuo* (Yield: 96%, 701 mg). Similarly, all other dimethyl indium derivatives were prepared. Analytical data are summarised in Table 4.

Crystallography

All measurements were made on a Rigaku AFC7S diffractometer using graphite monochromated Mo–Kα (λ = 0.71069 Å) radiation in the range $6 < 2\theta < 55.1°$. Crystallographic data, together with data collection and refinement details are given in Table 5. All the data were corrected for Lorentz and polarisation effects. The structure was solved by direct methods[28] and expanded using Fourier techniques.[29] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model.

Table 5 Crystallographic data for [{InMe$_2$(OC$_6$H$_4$OxMe$_2$)}$_2$] (**2a**)

Molecular formula	C$_{26}$H$_{36}$N$_2$O$_4$In$_2$
Formula weight	670.21
Crystal size/colour	0.2 × 0.2 × 0.2/colourless
Temperature (K)	293 (2)
Radiation Mo – Kα (Å)	0.71069
Crystal system	monoclinic
Space group	C2/c (# 15)
Cell parameters	
a (Å)	17.172 (4)
b (Å)	9.074 (4)
c (Å)	18.390 (5)
β (°)	105.60 (2)
V (Å^3)/Z	2759.8 (15)/4
Dcalc (g/cm^3)	1.613
Scan type	ω – 2θ
F$_{000}$/μ (mm^{-1})	1344/1.703
θ Range (°)	2.56 – 27.54
Limiting indices	$-12 \le h \le 22$; $0 \le k \le 11$; $-23 \le l \le 23$
Number of reflections/unique	3785/3184
No. of data \ restraints \ parameters	3184/0/160
Final R1, ωR2 indices [I > 2σ (I)]	0.0782, 0.1919
R1, ωR2 (all data)	0.0958, 0.2138
Goodness of fit on F^2	0.955

The final cycle of full matrix least squares refinement[30] on F^2 was based on 3184 observed reflections and 156 variable parameters and converged with unweighted and weighted agreement factors of:

$$R_1 = \Sigma||Fo|-|Fc||/\Sigma|Fo| = 0.0885$$

$$wR_2 = [\Sigma\,(w(Fo^2 - Fc^{2)2/}\Sigma\,(Fo^2)^2]^{1/2} = 0.2236$$

Neutral atom scattering factors were taken from Cromer and Waber.[31] All calculations were performed using Crystal Structure[32,33] crystallographic software package.

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