



Diorgano-gallium and -indium complexes with salen ligands: Synthesis, characterization, crystal structure and C–C coupling reactions

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ABSTRACT

The reactions of triorgano-gallium and -indium etherate with salen ligands in benzene afforded complexes of the type $[R_2MOC_6H_4CR'=NCH_2-]_2$, ($R/M/R' = Me/Ga/H$ (**1**), $Et/Ga/H$ (**2**), $Me/In/H$ (**3**), $Et/Ga/Me$ (**4**)) in nearly quantitative yields. These complexes have been characterized by elemental analysis, IR, UV–Vis, NMR (1H and $^{13}C\{^1H\}$) and mass spectral data. The organogallium complexes showed photoluminescence in blue-green region. The complex, $[(Me_2Ga)_2(O-(C_6H_4)CH=N-CH_2-)_2]$ on recrystallization from benzene–hexane and dichloromethane gave orthorhombic and monoclinic forms, respectively. Both the forms are dimeric with gallium atoms acquiring a distorted tetrahedral configuration defined by two methyl groups, phenolate oxygen and azomethene nitrogen. The complexes $[(Me_2Ga)_2(O-(C_6H_4)CH=N-CH_2-)_2]$ and $[(Me_2In)_2(O-(C_6H_4)CH=N-CH_2-)_2]$ have been employed as alkylating agent for C–C coupling reaction of 1-bromonaphthalene in presence of $PdCl_2(PPh_3)_2$.

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1. Introduction

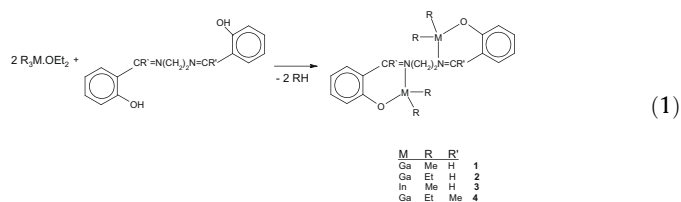
The chemistry of organo-gallium/-indium compounds with oxo ligands has been actively pursued for quite some time [1–3]. Interest in these compounds, particularly with internally functionalized ligands, appears to be due to their wide structural diversity [1], potential applications as catalyst [4,5] as well as molecular precursors for the preparation of metal oxide thin films [6–8] and photophysical properties [9–12].

The compounds of the type R_2ML ($R = \text{alkyl}$, $M = Ga$ or In ; $LH = \text{anionic oxo ligand}$) have been isolated as mono-, bi- and tri-nuclear derivatives with metal acquiring coordination number between four and six. The structural preferences in these complexes are governed by the nature of R , M and L [13–25]. Recently we have described the synthesis of diorgano-gallium/-indium complexes containing internally functionalized anionic oxo ligands [9,10,26,27]. These complexes have a centrosymmetric “ $M_2(\mu-O)_2$ ” core and show photoluminescence.

In view to assess photophysical and catalytic properties of bi- and high-nuclearity organo-gallium and -indium complexes lacking oxo-bridges, we have chosen salen ligands, although a few organo-gallium and -indium complexes with these ligands have been reported earlier [28–32]. In this report we describe the preparation of organo-gallium and -indium complexes with $salenH_2$ and $acenH_2$, their photophysical and catalytic properties and distortion isomerism in $[Me_2GaOC_6H_4CH=NCH_2-]_2$.

2. Results and discussion

Reactions of N,N' -ethylenebis(salicylideneimine) ($salenH_2$) and N,N' -ethylenebis(2-hydroxy- α -benzylideneimine) ($acenH_2$) with trialkylgallium etherate or trimethylindium etherate in 1:2 stoichiometry in benzene readily afforded bimetallic complexes, $[R_2MOC_6H_4CR'=NCH_2-]_2$, in nearly quantitative yield (Eq. (1)).



The electronic spectra displayed a number of bands attributable to transitions in the benzenoid ring (>300 nm) and in azomethine linkage (<300 nm). The $n \rightarrow \pi^*$ transition of the ligand (~ 370 nm) is red shifted (~ 10 nm) in organogallium complexes suggesting coordination of azomethine nitrogen to the metal atom. The $\nu C=N$ absorption in the IR spectra of the complexes appear at lower wave numbers relative to the free ligand. A strong band in the region $570\text{--}587\text{ cm}^{-1}$ has been attributed to $\nu Ga-C$ stretching absorptions [27].

The 1H and $^{13}C\{^1H\}$ NMR spectra of ligands and complexes showed expected signals and peak multiplicities. The methyl resonances of gallium complexes appear at higher field than that of the corresponding indium derivatives. The NCH_2 resonances both in the 1H and $^{13}C\{^1H\}$ NMR spectra of the complexes are shielded with respect to the signal for the corresponding ligands. This

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suggests coordination of azomethine nitrogen to the metal atom. As the consequence of the shift in electron density towards metal through nitrogen coordination, the $\text{CR}'=\text{N}$ ($\text{R}' = \text{H}$ or Me) resonance in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the organogallium complexes is deshielded (~ 5 ppm) as compared to the free ligand.

The mass spectrum of **1** exhibited multiplets at m/e 466 and 451 assignable to molecular ion and the parent ion minus one methyl group, respectively. These multiplets are consistent with the isotopic patterns for two gallium atoms in a molecule (^{69}Ga (60.4%), ^{71}Ga (39.6%).

2.1. Photophysical properties

Although 8-hydroxyquinolate (Ox) and azomethine coordinated complexes (e.g., $\text{Al}(\text{Ox})_3$) have been employed as organic light-emitting diodes (OLEDs) [33–38], organometallic complexes derived from chelating ligands are emerging as potential molecules for OLED applications [9–12,39,40].

The emission bands for the free ligands and complexes are summarized in Table 1. These bands both for ligand and complexes appeared in blue-green region (Fig. 1). On complexation there is a slight increase in quantum yield. The observed absorptions and emissions in diorganogallium complexes can be attributed to transitions localized on the salen ligands while enhanced quantum yields in the complexes could be due to the rigidity of the chelating ligand. The latter minimizes the loss of energy by a non-radiative pathway and consequently increases $\pi-\pi^*$ transition intensity.

2.2. Structure of $[\text{Me}_2\text{GaOC}_6\text{H}_4\text{CH}=\text{NCH}_2-]_2$ (**1**)

The complex crystallizes in orthorhombic (from benzene–hexane mixture) and monoclinic (from dichloromethane) forms representing an example of distortion isomerism in organogallium chemistry. This is the first example, to the best of our knowledge, of distortion isomerism in organogallium chemistry, although distortion isomerism for transition metal complexes is not uncommon [41]. The molecular structures of both the forms are similar except some variations in geometric parameters which are collected in Table 2. In orthorhombic form the molecule is distorted from C_i symmetry whereas monoclinic form, which crystallizes with a molecule of dichloromethane, retains this symmetry as illustrated in Fig. 2. The geometric parameters for the orthorhombic form are in conformity with the one reported earlier by Trotter and co-workers [28].

The molecule (Fig. 3) essentially comprises of two four-coordinated dimethylgallium fragments containing five membered chelating ligands and these two fragments are linked through a $-\text{CH}_2-\text{CH}_2-$ spacer. Each gallium atom has a distorted tetrahedral configuration defined by two methyl groups and phenolic oxygen and azomethine nitrogen atoms. The Ga–C, Ga–O and Ga–N distances are well in agreement with the reported values [3,10,28].

3. Cross alkylation reactions

Organoindium compounds have been employed for cross-coupling of arylhalides in the presence of palladium chloride catalysts

Table 1

Excitation and emission data of salen ligands and their diorganogallium complexes in dichloromethane.

Compounds	Excitation λ in nm	Emission λ in nm	Quantum yield (η) in %
$[\text{HO}(\text{C}_6\text{H}_4)\text{CH}=\text{NCH}_2-]_2$	365	470	0.4
$[\text{HO}(\text{C}_6\text{H}_4)\text{CMe}=\text{NCH}_2-]_2$	435	473	3.0
$[\text{Me}_2\text{GaO}(\text{C}_6\text{H}_4)\text{CH}=\text{NCH}_2-]_2$	412	462	1.2
$[\text{Et}_2\text{GaO}(\text{C}_6\text{H}_4)\text{CH}=\text{NCH}_2-]_2$	335	485	0.1
$[\text{Et}_2\text{GaO}(\text{C}_6\text{H}_4)\text{CMe}=\text{NCH}_2-]_2$	355	475	1.0

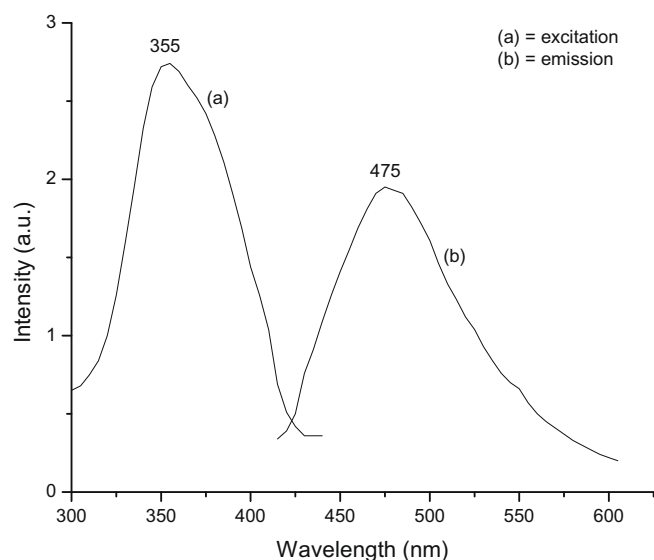


Fig. 1. Excitation spectra (a) and emission spectra (b) of $[\text{Et}_2\text{GaO}(\text{C}_6\text{H}_4)\text{C}(\text{CH}_3)=\text{N}-\text{CH}_2-]_2$ recorded in dichloromethane solution.

Table 2

Selected geometric parameters (\AA , $^\circ$) for $[(\text{Me}_2\text{Ga})_2(\text{O}-\text{C}_6\text{H}_4)\text{CH}=\text{N}-\text{CH}_2-]_2$ recrystallized in benzene–hexane mixture and CH_2Cl_2 solvents.

	Orthorhombic		Monoclinic
	Literature ^a	This work	This work
Ga1–O1	1.869 (2)	1.867 (4)	1.895 (3)
Ga2–O2	1.874 (2)	1.873 (4)	–
Ga1–N1	2.026 (3)	2.022 (5)	2.048 (3)
Ga2–N2	2.035 (3)	2.029 (5)	–
Ga1–C10	1.950 (5)	1.921 (7)	1.955 (4)
Ga1–C9	1.948 (6)	1.942 (7)	1.951 (4)
Ga2–C19	1.959 (5)	1.929 (6)	–
Ga2–C20	1.938 (5)	1.931 (6)	–
O1–Ga1–C10	106.5 (3)	111.5 (3)	108.90 (18)
O1–Ga1–C9	105.7 (3)	105.7 (3)	108.51 (19)
O2–Ga2–C19	112.6 (2)	111.4 (3)	–
O2–Ga2–C20	107.3 (2)	107.0 (3)	–
O1–Ga1–N1	94.0 (1)	94.04 (18)	91.99(11)
O2–Ga2–N2	92.7 (1)	92.41 (18)	–
C10–Ga1–C9	124.6 (4)	124.6 (4)	127.6 (2)
C19–Ga2–C20	123.8 (3)	125.5 (3)	–
C10–Ga1–N1	110.2 (3)	106.2 (2)	105.65 (18)
C9–Ga1–N1	106.3 (2)	110.5 (3)	108.37 (16)
C19–Ga2–N2	104.4 (2)	103.8 (3)	–
C20–Ga2–N2	111.8 (2)	111.7 (3)	–
C11–O2–Ga2	126.6 (2)	127.2 (4)	–
C1–O1–Ga1	128.1 (2)	128.4 (4)	126.6 (2)
C7–N1–Ga1	122.2 (2)	122.7 (4)	122.0 (2)
C8–N1–Ga1	119.6 (3)	119.3 (4)	119.5 (3)
C17–N2–Ga2	121.6 (2)	121.8 (4)	–
C18–N2–Ga2	118.8 (3)	118.1 (4)	–

^a Ref. [28].

[4,5,42]. In general mononuclear organoindium complexes are better alkylating agents than the binuclear complexes containing “ $\text{In}_2(\mu\text{-O})_2$ ” core [42]. The bimetallic salen complexes described here are akin to mononuclear compounds, they may be useful in cross-coupling reactions. Thus in a preliminary experiment, 1-bromonaphthalene is readily methylated to 1-methylnaphthalene (^1H NMR (in CDCl_3) δ : 2.75 (s, Me–)) by **3** in the presence of $\text{PdCl}_2(\text{PPh}_3)_2$ as a catalyst. The reaction of $[\text{PdCl}_2(\text{PPh}_3)_2]$ with **3** in a separate experiment (Eq. (2)), has shown the formation of *trans*- $[\text{PdClMe}(\text{PPh}_3)_2]$ (^1H NMR (in CDCl_3) δ : -0.01 (t, 6.5 Hz, Pd–Me); $^{31}\text{P}\{^1\text{H}\}$ 30.2 ppm). Similarly other palladium complexes,

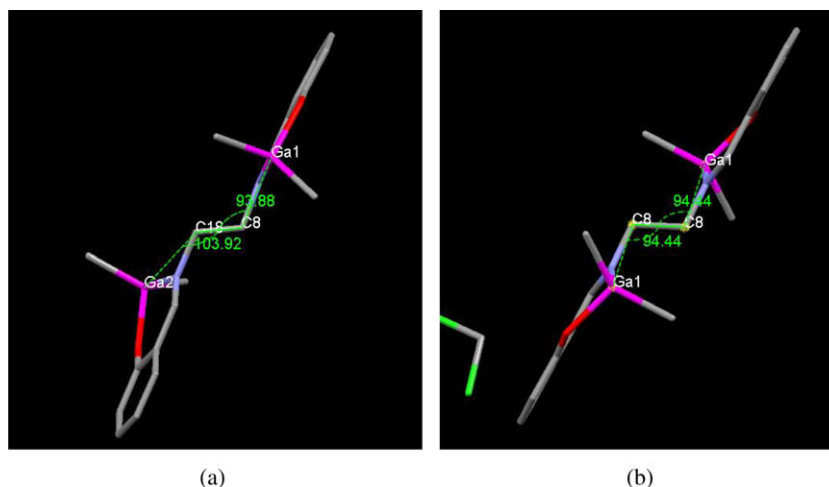
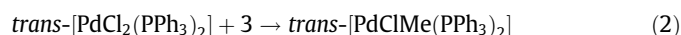


Fig. 2. Line drawing of orthorhombic (a) and monoclinic (b) forms of $[\text{Me}_2\text{GaO}(\text{C}_6\text{H}_4)\text{CH}=\text{NCH}_2-]_2$.

e.g. $[\text{Pd}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{PET}_3)_2]$ can be methylated to $[\text{Pd}_2\text{Me}_2(\mu\text{-Cl})_2(\text{PET}_3)_2]$ (^1H NMR (in CDCl_3) δ : 0.59 (br s, Pd-Me); $^{31}\text{P}\{^1\text{H}\}$ NMR (in CDCl_3) δ : 32.8 ppm) [43].



4. Experimental

4.1. Materials and physical measurements

All experiments involving organo-gallium/-indium compounds were carried out in anhydrous conditions under a nitrogen atmosphere using Schlenk techniques. Solvents were dried by standard methods. The $\text{R}_3\text{Ga} \cdot \text{OEt}_2$ ($\text{R} = \text{Me}, \text{Et}$) were prepared from gallium-magnesium alloy and alkyl iodide in diethyl ether while $\text{Me}_3\text{In} \cdot \text{OEt}_2$ was obtained by a reaction between anhydrous InCl_3 and MeMgI in ether [44]. Ether contents in each preparation were evaluated by ^1H NMR integration.

Infrared spectra were recorded as KBr plates on a Bomem MB-102 FT IR spectrometer. The NMR spectra were recorded on a Bruker Avance-II 300 spectrometer in 5 mm tubes as CDCl_3 solutions. Chemical shifts were referenced to internal chloroform peak (δ 7.26 and 77.0 ppm for ^1H and $^{13}\text{C}\{^1\text{H}\}$, respectively). Mass spectra were recorded on a Waters Q-TOF micro-mass (YA-105) time of flight mass spectrometer. Electronic spectra were recorded in ben-

zene or dichloromethane on a Chemito Spectroscan UV-double beam spectrophotometer. Emission spectra were measured in deoxygenated solvents on a Hitachi F-4010 Fluorescence spectrophotometer.

4.2. Synthesis

4.2.1. *N,N'*-ethylenebis(salicylideneimine)

To a benzene solution (50 cm^3) of salicylaldehyde (13.18 g, 108 mmol), a solution of ethylenediamine (3.24 g, 54 mmol) was added with stirring and the whole was refluxed on a Dean Stark apparatus for 5 h. The solvent was evaporated under vacuum and the yellow residue (yield 95%, 13.92 g) was recrystallised from benzene (m.p. 125 $^\circ\text{C}$); IR: $\nu_{\text{C}=\text{N}}$ 1635 cm^{-1} . UV-Vis (in benzene) λ_{max} (in nm): 233, 258, 290, 318, 377. ^1H NMR in CDCl_3 δ : 3.92 (s, 4H, NCH_2-); 6.87 (t, 7 Hz, 2H, CH-4); 6.96 (d, 8 Hz, 2H, CH-3); 7.22–7.33 (m, 4H, CH-5, 6); 8.35 (s, 2H, $\text{N}=\text{CH}-$); 13.28 (s, 2H, OH). $^{13}\text{C}\{^1\text{H}\}$ in CDCl_3 δ : 59.7 (s, NCH_2); 116.9, 118.6, 131.5, 132.4, 161.0, 166.5.

4.2.2. Preparation of *N,N'*-ethylenebis(2-hydroxy- α -benzylideneimine)

Prepared similarly to the above ligand using ethylenediamine and 2-hydroxy acetophenone and recrystallised from benzene-ethanol mixture in 93% yield, m.p. 181 $^\circ\text{C}$. IR: $\nu_{\text{C}=\text{N}}$ 1610 cm^{-1} . UV-Vis (in benzene) λ_{max} (in nm): 231, 257, 277, 320 and 369. ^1H NMR in CDCl_3 δ : 2.39 (s, 6H, CMe); 3.98 (s, 4H, NCH_2-); 6.80 (dt, 1 Hz (d), 7.5 Hz (t, 2H)); 6.91 (dd, 1 Hz (d), 8 Hz (d), 2H); 7.29 (td, 1 Hz (d), 8 Hz (t), 2H); 7.54 (dd, 1.5 Hz, 7 Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ in CDCl_3 δ : 14.8 (s, CMe); 50.1 (s, NCH_2); 117.4, 118.5, 119.4, 128.2, 132.5, 163.2, 172.8.

4.2.3. $[\text{Me}_2\text{GaO}(\text{C}_6\text{H}_4)\text{CH}=\text{NCH}_2-]_2$ (**1**)

To a benzene solution (25 cm^3) of trimethylgallium etherate (2.0 g, containing 1.03 g (9.0 mmol) Me_3Ga), was added a solution of *N,N'*-ethylenebis(salicylideneimine) (1.2 g, 4.48 mmol) with stirring which continued for 3 h. The solvent was evaporated under a reduced pressure to give a yellow crystalline solid (2.05 g, 98%) which was recrystallised from dichloromethane-hexane as a colorless crystalline solid, m.p. 170 $^\circ\text{C}$. Anal. Calc. $\text{C}_{20}\text{H}_{26}\text{Ga}_2\text{N}_2\text{O}_2$: C, 51.5; H, 5.6; N, 6.0; Ga, 29.9. Found: C, 50.1; H, 5.7; N, 5.9; Ga, 29.5% (a slight difference between the calculated and observed values of analysis may be due to operational difficulty in handling air and moisture sensitive compounds in the analytical laboratory). IR: $\nu_{\text{C}=\text{N}}$, 1623; Ga–C, 585 cm^{-1} . UV-Vis (in CH_2Cl_2) λ_{max} : 241, 281, 385 nm. ^1H NMR in CDCl_3 δ : –0.20 (s, 12H, Me_2Ga); 3.80 (s,

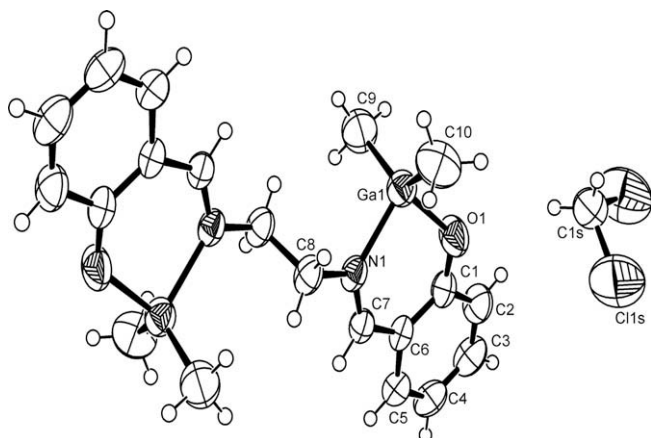


Fig. 3. Crystal structure of $[(\text{Me}_2\text{Ga})_2(\text{O}-(\text{C}_6\text{H}_4)\text{CH}=\text{N}-\text{CH}_2-)]_2$. CH_2Cl_2 grown in dichloromethane solvent.

4H, NCH₂-); 6.63 (t, 7.8 Hz, 2H); 6.83 (d, 8 Hz, 2H); 6.99 (d, 8 Hz); 7.35 (t, 7.5 Hz, 2H); 7.92 (s, 2H, N=CH-). ¹³C{¹H} (in CDCl₃) δ: -6.6 (s, Me₂Ga); 57.3 (s, NCH₂); 116.7, 117.6(s), 122.4(s), 135.3 (s), 137.0 (s) 166.7 (s), 171.5 (CH=N). Mass *m/e*: 466 (M⁺); 451 (M-Me); 351 [MeGaOC₆H₄CH=NCH₂CH₂N=CHC₆H₄O]⁺; 335 (GaOC₆H=CH=NCH₂CH₂N=CHC₆H₄O); 269 (L); 247 ([Me₂GaOC₆H₄CH=NCH₂CH₂)⁺].

4.2.4. [Et₂GaO(C₆H₄)CH=NCH₂]₂ (2)

Prepared similar to **1** in 96% yield, m.p. 105 °C. Anal. Calc. for C₂₄H₃₄Ga₂N₂O₂: C, 55.2; H, 6.6; N, 5.4; Ga, 26.7. Found: C, 54.0; H, 6.7; N, 5.6; Ga, 26.9%. IR: νC=N, 1625; Ga-C, 570 cm⁻¹. UV-Vis (in CH₂Cl₂) λ_{max}: 244, 275, 392 nm. ¹H NMR (in CDCl₃) δ: 0.52 (m, 8H, GaCH₂-); 1.11 (t, 8 Hz, 12H, GaCH₂Me); 3.78 (s, 4H, NCH₂-); 6.62 (t, 7.5 Hz, 2H); 6.86 (d, 8 Hz, 2H); 6.99 (d, 8 Hz, 2H); 7.35 (t, 7.5 Hz, 2H); 8.00 (s, 2H, N=CH-). ¹³C{¹H} (in CDCl₃) δ: 3.8 (s, GaCH₂); 9.7 (s, GaCH₂Me); 57.6 (s, NCH₂-); 116.7(s), 117.7 (s), 122.3(s), 135.3 (s), 137.1 (s), 167.6(s), 171.8 (s, -CH=N-).

4.2.5. [Me₂InO(C₆H₄)CH=NCH₂]₂ (3)

Prepared similar manner to **1** in 95% yield, since the complex was sparingly soluble in organic solvents, it was washed thoroughly with benzene and dried *in vacuo*. m.p. 240 °C (decompose). Anal. Calc. for C₂₀H₂₆In₂N₂O₂: C, 43.2; H, 4.7; N, 5.0; In, 41.3. Found C, 44.2; H, 4.5; N, 4.7; In, 41.2%. IR: νC=N 1600 cm⁻¹. ¹H NMR (in dmso-*d*₆) δ ppm: -0.16 (s, 12H, Me₂In); 3.85 (s, 4H, NCH₂-); 6.62 (t, 7.5 Hz, 2H); 7.01 (d, 7 Hz, 2H); 7.10 (dd, 4H); 8.26 (s, 2H, N=CH).

4.2.6. [Et₂GaO(C₆H₄)CMe=NCH₂]₂ (4)

Prepared similar to **1** in 96% yield, m.p. 185 °C. Anal. Calc. for C₂₆H₃₈Ga₂N₂O₂: C, 56.8; H, 7.0; N, 5.1; Ga, 25.3. Found: C, 56.4; H, 7.1; N, 5.4; Ga, 25.0%. IR: νC=N, 1602; Ga-C, 587 cm⁻¹. UV-Vis (in CH₂Cl₂) λ_{max}: 233, 262, 275, 325 (sh), 378 nm. ¹H NMR (in CDCl₃) δ: 0.42 (m, 8H, GaCH₂-); 1.05 (t, 8 Hz, 12H, GaCH₂Me); 2.58 (s, 6H, CMe); 3.82 (s, 4H, NCH₂-); 6.71 (t, 7.0 Hz, 2H); 6.93

(d, 7.8 Hz, 2H); 7.34 (m, 2H); 7.43 (d, 8 Hz, 2H). ¹³C{¹H} (in CDCl₃) δ: 3.1 (s, GaCH₂-); 9.9 (s, GaCH₂Me); 18.5 (s, CMe); 49.1 (s, NCH₂); 116.7 (s), 122.2 (s), 123.6 (s), 130.4 (s), 135.0 (s) 166.3 (s), 177.6 (s, -CMe=N).

5. X-ray crystallography

Intensity data for [Me₂GaO(C₆H₄)CH=NCH₂]₂, crystallized from benzene (orthorhombic) and dichloromethane (monoclinic) were collected on a Rigaku AFC 7S diffractometer fitted with Mo Kα radiation so that θ_{max} = 27.5°. The structures were solved by direct methods [45] and refinement was an F² [45] using data that had been corrected for absorption effects with an empirical procedure [46] with non hydrogen atoms modeled with anisotropic displacement parameter with hydrogen atoms in their calculated positions. Molecular structures were drawn using ORTEP [47]. Crystallographic and structural determination data are listed in Table 3.

6. Cross alkylation of 1-bromonaphthalene

In a typical experiment, a benzene solution of 1-bromonaphthalene (1.19 g, 2.82 mmol) containing [Me₂InO(C₆H₄)CH=NCH₂]₂ (**3**) (1.57 g, 2.82 mmol) and [PdCl₂(PPh₃)₂] (45 mg, 0.06 mmol) was refluxed for 2 h. After cooling the reaction mixture to room temperature, it was treated with an excess of 10% HCl (25 ml) which lead to separation of two phases. The organic phase was separated and aqueous phase was washed with ether (2 × 10 ml) and combined with the organic phase which was dried in vacuum to give a pale yellow liquid which was distilled under vacuum to yield a colorless liquid (0.44 g, 55%), identified as 1-methylnaphthalene by ¹H NMR spectroscopy.

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Appendix A. Supplementary material

CCDC 717099 and 717100 contain the supplementary crystallographic data for orthorhombic and monoclinic forms. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.03.029](https://doi.org/10.1016/j.jorganchem.2009.03.029).

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Table 3

Crystallographic and structural refinement data of [Me₂GaO-(C₆H₄)CH=N-CH₂]₂.

	Recrystallised from benzene-hexane	Recrystallised from dichloromethane
Formula	C ₂₀ H ₂₆ Ga ₂ N ₂ O ₂	C ₂₀ H ₂₆ Ga ₂ N ₂ O ₂ · CH ₂ Cl ₂
<i>M</i>	465.87	550.79
<i>T</i> (K)	298	298
Colour	Yellow	Yellow
Size	0.1 × 0.4 × 0.5	0.2 × 0.4 × 0.5
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pbc</i>	<i>C12/c1</i>
<i>a</i> (Å)	19.700 (5)	22.400 (7)
<i>b</i> (Å)	22.830 (7)	9.117 (2)
<i>c</i> (Å)	9.494 (2)	13.772 (3)
β (°)	90.00	117.28 (2)
<i>V</i> (Å ³)	4270 (2)	2499.6 (11)
<i>Z</i>	8	4
<i>d</i> _{calc} (g cm ⁻³)	1.449	1.464
μ (mm ⁻¹)/ <i>F</i> (000)	2.539/1904	2.387/1120
θ for data collection (°)	2.54–27.57	2.69–27.55
Limiting indices	-14 ≤ <i>h</i> ≤ 25 0 ≤ <i>k</i> ≤ 29 -6 ≤ <i>l</i> ≤ 12	-16 ≤ <i>h</i> ≤ 29 -11 ≤ <i>k</i> ≤ 6 -17 ≤ <i>l</i> ≤ 15
Absorption correction	Psi-scan	Psi-scan
Refinement method	Full matrix least squares on <i>F</i> ² > 0	Full matrix least squares on <i>F</i> ² > 0
No. of unique reflections	4927	2878
No. of observed reflections with <i>I</i> > 2σ(<i>I</i>)	2246	1844
Data/restraints/parameters	4927/0/247	2878/0/166
Final <i>R</i> ₁ , ω <i>R</i> ₂ indices	0.053/0.169	0.042/0.107
<i>R</i> ₁ , ω <i>R</i> ₂ (all data)	0.163/0.169	0.084/0.125

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