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Synthesis and structure of novel chiral amido-imine complexes of aluminum, gallium, and indium

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The reactions of 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-BIAN, **1**) with tri-*iso*-butylaluminum, triethylgallium or trimethylindium give the novel amido-imine complexes (Bu^i—dpp-BIAN)$AlBu^i{}_2$ (**4**), (Et—dpp-BIAN)$GaEt_2$ (**5**), and (Me—dpp-BIAN)$InMe_2$ (**6**), respectively. The reaction of (dpp-BIAN)AlI(Et_2O) (**7**) with allyl bromide affords analogous chiral amido-imine derivative (All—dpp-BIAN)AlBrI (**8**). Hydrolysis of **8** affords the amino-imino compound (All—dpp-BIAN)H (**9**). The new compounds **4—6**, **8**, and **9** have been characterized by ^1H NMR and IR spectroscopy. The molecular structures of **5**, **6**, and **9** were determined by single crystal X-ray analysis.

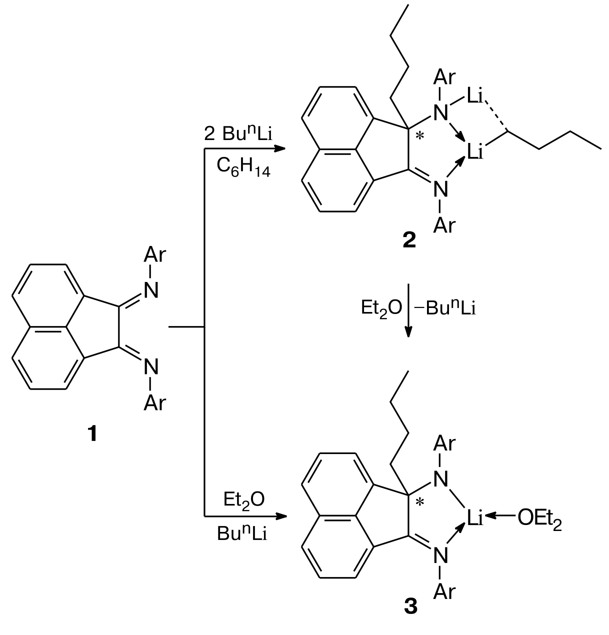
Key words: aluminum, gallium, indium, diimines, chiral ligands, X-ray diffraction analysis.

The progress in metallorganic and coordination chemistry is largely enabled by versatility of organic ligands used for the synthesis of metallocomplexes. Over the last years there has been much research activity focused on metal diimine complexes and, in particular, the derivatives of acenaphthene-1,2-diimines (BIAN), which exhibit rather interesting chemical properties. The transition metal complexes with BIAN ligands catalyze alkyne hydrogenation,[1] C—C bond generating reactions,[2] cycloisomerization,[3] and are especially effective in polymerization of olefins[4] and acrylic monomers.[5]

During recent years, we have synthesized the complexes of Group 1, 2, 13, 14, and 15 metals with BIAN ligands. Magnesium and aluminum complexes with 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (**1**, dpp-BIAN) are highly reactive towards a wide variety of organic species,[6] *i.e.*, terminal alkynes, ketones, nitriles, halo-substituted hydrocarbons; they also display good activity as catalysts of ring opening polymerization of lactide.[7]

Lithium complexes containing chiral amido-imine ligand are obtained by reacting dpp-BIAN with butyllithium (Scheme 1).[8] The reactions involve the addition of Bu^nLi to one of the two C=N double bonds of a ligand, where an *n*-butyl radical adds to the imine carbon and a lithium atom — to the nitrogen, yielding the lithium salt of unsymmetrical chelating amido-imine ligand.

Scheme 1



An anionic amido-imine ligand [Bu^n—dpp-BIAN]$^-$ can be transferred from lithium to other metals, *e.g.*, germanium(II)[8] and zinc(II).[9] The analogous alkaline earth metal complexes are also known. In particular, (dpp-BIAN)$Mg(thf)_3$ interacts with ethyl halides in hexane to yield amido-imine complex [(Et—dpp-BIAN)-

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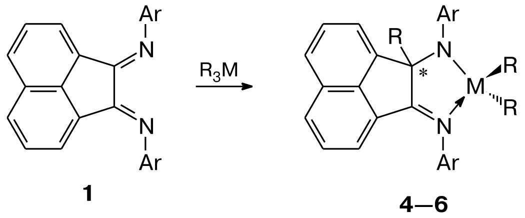
$MgX(thf)_n$].[6g] The same products are formed in the reactions of ligand **1** with Grignard reagents.

Employment of such chelating systems give rise to new synthetic routes offering an access to metallorganic reagents for synthetic applications. For example, chiral aluminum complex (imino-amido)$AlMe_2$ synthesized by the reaction between α-diimine Ar—N=C(Me)—C(Me)=N—Ar (Ar = 2,6-$Pr^i_2C_6H_3$) and Me_3Al (1 : 1) or methylalumoxane (1 : 3)[10] was found to catalyze ethylene polymerization. This makes the chemistry of complexes with chiral ligands attractive from a practical perspective. Here we describe synthesis and structure of the novel chiral amido-imine complexes of Group 13 metals.

Results and Discussion

Synthesis and identification of compounds. New chelate amido-imine complexes (Bu^i—dpp-BIAN)$AlBu^i_2$ (**4**), (Et—dpp-BIAN)$GaEt_2$ (**5**), and (Me—dpp-BIAN)$InMe_2$ (**6**) were prepared by reacting diimine **1** with triisobutylaluminum, triethylgallium, and trimethylindium, respectively (Scheme 2).

Scheme 2



Ar = 2,6-$Pr^i_2C_6H_3$
M = Al, R = Bu^i (**4**); M = Ga, R = Et (**5**); M = In, R = Me (**6**)

It should be noted that the reactions occur only in non-coordinating solvents, such as toluene or hexane. Coordinating solvents (diethyl ether or THF) are involved in the formation of $R_3M{\leftarrow}OEt_2$ adducts, which hampers the addition of metal alkyls to diimine **1**. Substitution of a coordinating solvent with toluene does not afford adduct dissociation leading to R_3M and dpp-BIAN addition product. The above data suggest that the alkyl addition over C=N bond begins with the coordination of dpp-BIAN ligand nitrogens by a Group 13 metal. Complexes **4**, **5**, and **6** were synthesized in toluene and then isolated by recrystallization from hexane as red colored prisms in 92, 87, and 83% yield, respectively. They were characterized by IR and NMR, including $^1H,^1H$-COSY technique. The structures of complexes **5** and **6** were determined by X-ray diffraction and are shown in Figs 1 and 2, respectively. Details of crystal data, data collection and structure refinement are listed in Table 1. Selected bond lengths and bond angles for structures **5** and **6**, as well as the corresponding values for dpp-BIAN, are collected in Table 2.

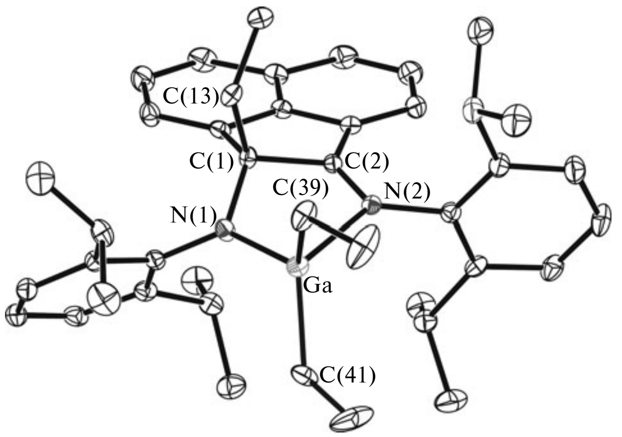


Fig. 1. Molecular structure of complex **5**. Thermal ellipsoids 50%. Hydrogen atoms are omitted.

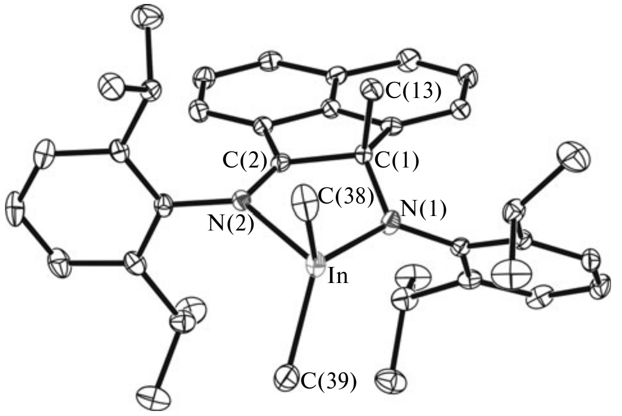


Fig. 2. Molecular structure of complex **6**. Thermal ellipsoids 50%. Hydrogen atoms are omitted.

The molecule of diimine dpp-BIAN[6d] lies on a crystallographic twofold rotation axis passing through the C—C bond linking to six-membered rings of a naphthalene moiety. The distances C(1)—N(1) and C(2)—N(2) (1.282(4) Å) match with the double C=N bond, and C(1)—C(2) distance (1.534(6) Å) is close to the value of a single C—C bond.

Attachment of alkyl group to the imine carbon of diimine **1** generates a chiral center at C(1) in molecules **5** and **6** and their symmetry is thus distorted. Unlike chiral amido-imine complexes of zinc[9] and magnesium,[6g] with a unit cell containing both isomers (*R* and *S*), compounds **5** and **6** crystallize as a conglomerate (a mechanical mixture of enantiomers).[11] Figures 1 and 2 show *S* isomer of **5** and *R* isomer of **6**, respectively.

It is noteworthy that crystal **6** exhibits lamellar racemic twinning[11b] as indicated by Flack parameter (0.466(7)),[12] whereas in crystal **5** only one enantiomer is present (Flack parameter is 0.000(1)).

Non-symmetry of structures **5** and **6** is manifested in different C—N bond distances in diimine fragments of

Table 1. Crystallographic data and X-ray diffraction experiment parameters for structures **5**, **6**, and **9**

Parameter	**5**	**6**	**9**
Molecular formula	$C_{42}H_{55}GaN_2$	$C_{39}H_{49}InN_2$	$C_{39}H_{46}N_2$
Molecular weight	657.60	660.62	542.78
T/K	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$	$P2_1/c$
a/Å	10.1514(5)	9.8767(3)	18.8454(7)
b/Å	16.6995(8)	16.0203(5)	17.0502(6)
c/Å	10.8457(5)	10.8136(4)	20.2102(8)
β/deg	98.8030(10)	96.0516(6)	99.3680(10)
V/Å^3	1816.94(15)	1701.48(10)	6407.3(4)
Z (Z')	2 (1)	2 (1)	8 (1)
d/g cm^{-3}	1.202	1.289	1.125
μ/mm^{-1}	0.788	0.723	0.064
F(000)	704	692	2352
θ_{max}/deg	29.00	29.00	26.00
Number of measured reflections	17434	17172	38230
Number of independent reflections (R_{int})	9368 (0.0350)	8767 (0.0244)	12584 (0.0363)
GOF(F^2)	0.991	0.975	1.030
$R_1/_wR_2$ ($I > 2\sigma(I)$)	0.0396/0.0831	0.0243/0.0571	0.0437/0.1049
$R_1/_wR_2$ (based on all reflections)	0.0495/0.0879	0.0263/0.0585	0.0678/0.1131
Residual electron density/e • Å^{-3}, ρ_{max}/ρ_{min}	0.436/–0.354	0.593/–0.746	0.305/–0.366

Table 2. Selected bond lengths (d) and bond angles (ω) in compounds **1**,[6d] **5**, **6**, and **9**

Parameter	**1**	**5**	**6**	**9**
Bond		d/Å		
M—N(1)	—	1.919(1)	2.123(1)	—
M—N(2)	—	2.139(1)	2.323(1)	—
C(1)—N(1)	1.282(4)	1.465(3)	1.457(3)	1.489(2)/1.492(2)^a
C(2)—N(2)	1.282(4)	1.279(3)	1.283(2)	1.272(1)/1.271(1)^a
C(1)—C(2)	1.534(6)	1.554(3)	1.551(2)	1.554(2)/1.545(2)^a
C(1)—C(13)	—	1.563(3)	1.555(2)	1.542(2)/1.543(2)^a
M—R^1	—	1.994(3)^b	2.170(2)^c	—
M—R^2	—	1.983(3)^d	2.158(2)^e	—
Angle		ω/deg		
N(1)—M—N(2)	—	82.14(8)	76.62(6)	—
N(1)—M—R^1	—	117.6(1)^b	116.7(1)^c	—
N(1)—M—R^2	—	109.0(1)^d	119.2(1)^e	—
N(2)—M—R^1	—	105.0(1)	103.4(1)	—
N(2)—M—R^2	—	115.1(2)	108.7(1)	—
R^1—M—R^2	—	121.3(2)	120.1(1)	—

[a] Values for the second molecule.

[b] Ga—C(39).

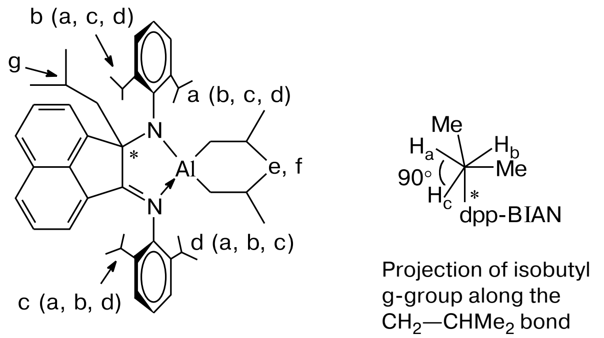
[c] In—C(38).

[d] Ga—C(41).

[e] In—C(39).

molecules. The C(2)—N(2) bonds in **5** (1.279(3) Å) and **6** (1.283(2) Å) are double and are essentially shorter than C(1)—N(1) (1.465(3) and 1.457(3) Å, respectively). The C(1)—C(2) distances in **5** (1.554(3) Å) and **6** (1.551(2) Å) are comparable with a single bond distance C(1)—C(2) in the free ligand dpp-BIAN (1.534(6) Å). In structures **5** and **6**, a five-membered ring $MN_2C(1)C(2)$ adopts a distorted envelope conformation with the N(1) atom displaced ~0.59 Å out of the ring plane.

Both molecules **5** and **6** have distorted tetrahedral coordination around metal centers linked to two alkyl carbons and two nitrogens of the chelating amido-imine



4

Projection of isobutyl g-group along the CH_2—$CHMe_2$ bond

Fig. 3. Structure of complex (Bu^i—dpp-BIAN)AlBu$^i_2$ (**4**) from ^{1}H NMR and ^{1}H,^{1}H-COSY data.

ligand (see Figs 1 and 2). Amido and imino nitrogens differ in their M—N bond lengths (M = metal). The amido bond M—N(1) (**5**: Ga—N(1), 1.9190(19) Å; **6**: In—N(1), 2.1228(17) Å) is substantially shorter compared to coordination bond M—N(2) (**5**: Ga—N(2), 2.1389(17) Å; **6**: In—N(2), 2.3229(16) Å).

Although compound **4** was not characterized by X-ray diffraction, its structure shown in Fig. 3 was proved absolutely by ^{1}H NMR data.

The isobutyl group attached to dpp-BIAN (g-group, see Fig. 3) gives a complex signal in the ^{1}H NMR spectrum (Fig. 4). Two methylene protons (H_a and H_b) are nonequivalent due to bonding to the nonsymmetrical carbon atom of the five-membered ligand ring. As a result, they are found at δ 3.31—2.60 as two signals showing large spin-spin splitting (doublet (H_a) at δ 3.28, J = 13.6 Hz and double doublet (H_b) at δ 2.66, J = 13.6 and 8.8 Hz). This set of signals can be interpreted as follows: the doublet is due to the H_a proton which in the projection of g-group (see Fig. 3) makes an angle of ~90° with the methyne proton H_c and, hence, does not interact with it producing only the doublet (resulting from coupling with H_b proton). The H_b proton in the projection is rotated 150° with respect to H_c proton and gives a double doublet (coupling with H_a and H_c).

Since the addition of alkyl group renders structures **4**—**6** chiral by generating a nonsymmetric carbon atom, all aromatic and methine protons, and also all the eight methyl groups are nonequivalent (see Fig. 4, *a*). Four methine protons appear as four septets at δ 4.9—3.0 (see Fig. 4, *b*), and eight methyl groups — as eight doublets in the 1.8 to –0.4 region (see Fig. 4, *c*).

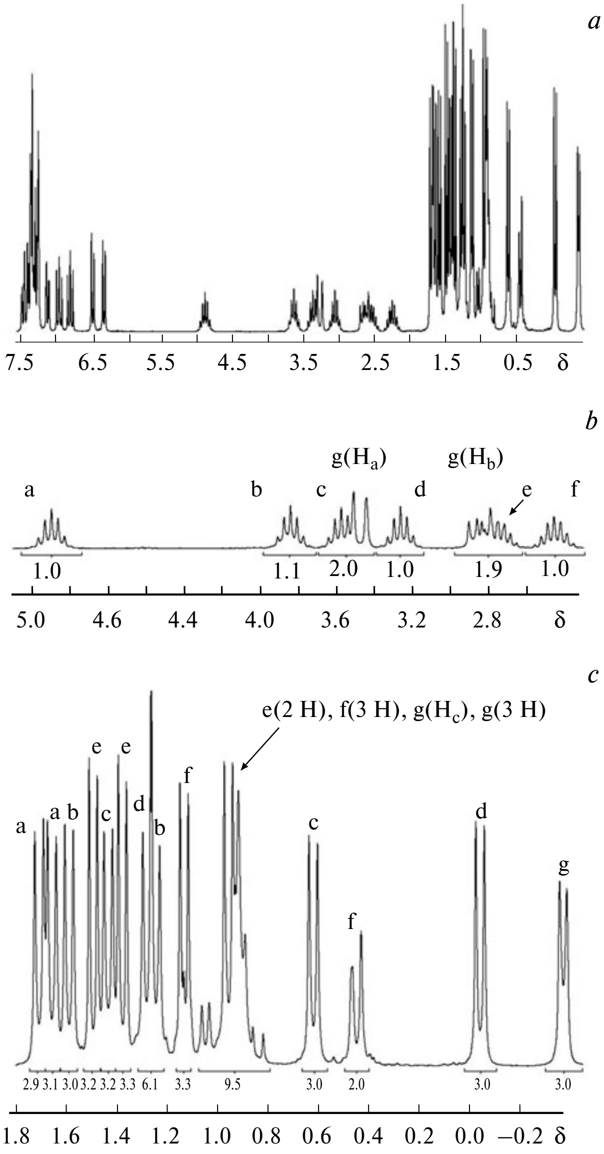


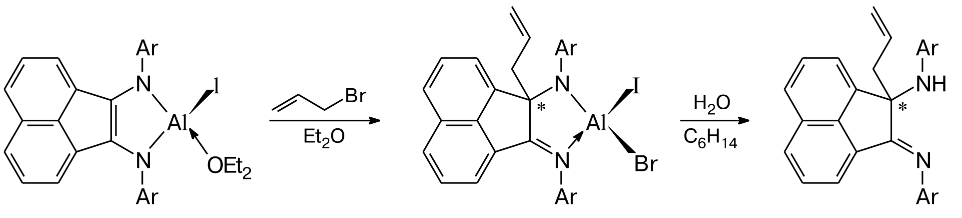
Fig. 4. ^{1}H NMR spectrum of compound (Bu^i—dpp-BIAN)-AlBu$^i_2$ (**4**) (C_6D_6, 200 MHz) (*a*) and assignment of signals from aliphatic protons (*b* and *c*). Proton labeling is shown in Fig. 3.

In the similar manner with the magnesium complexes,[6g] Group 13 metal complexes with nonsymmetrical amido-imine ligands can be obtained by reactions of dpp-BIAN dianion derivatives with alkyl halides. Such reaction between (dpp-BIAN)AlI(Et_2O) (**7**) and allyl bromide (AllBr) leads to amido-imine complex (All—dpp-BIAN)AlBrI (**8**) (Scheme 3). Complex **8** was isolated from ether as orange crystals in 55% yield and characterized by IR and NMR (including ^{1}H,^{1}H-COSY). Compound **8** was not examined by X-ray diffraction; its structure shown in Scheme 3 was tentatively identified based on the ^{1}H NMR data. The hydrolysis of complex **8** yielded (78%) amino-imine **9** (see Scheme 3), which was isolated from hexane as yellow crystals and characterized by NMR.

In the field of aliphatic protons the ^{1}H NMR spectrum of **9** (Fig. 5) shows half of signals as compared to the spectrum of complex **8**.

Two signals from the methine protons of isopropyl groups appear as partially overlapping septets at δ 3.46 and 3.33. Four doublets due to methyl moities of isopropyl groups instead of the eight expected are found at

Scheme 3



7 **8** **9**

Ar = 2,6-$Pr^i_2C_6H_3$

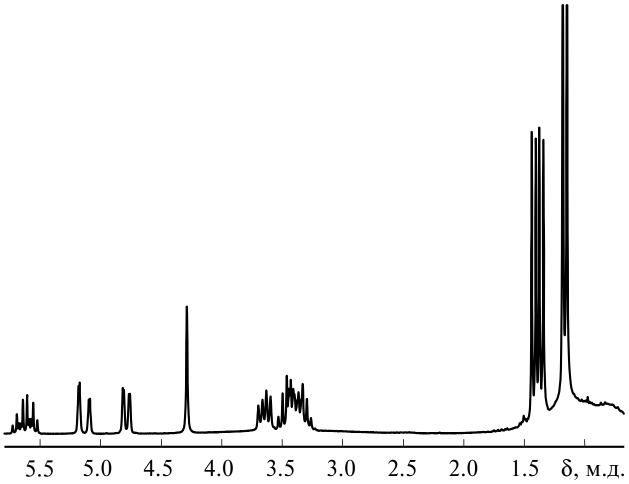


Fig. 5. ^{1}H NMR spectrum of compound (All—dpp-BIAN)H (**9**) (C_6D_6, 200 MHz). The δ field containing signals from aromatic protons is omitted.

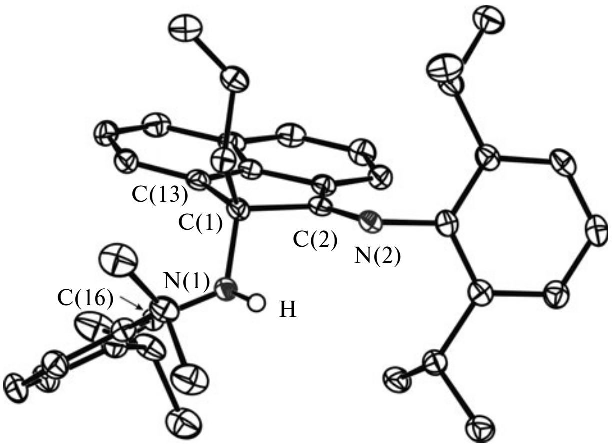


Fig. 6. Molecular structure of compound **9**. Thermal ellipsoids 50%. Hydrogen atoms are omitted except one bound to N(1).

δ 1.5—1.1. The allylic methylene protons in the α-position to the chiral center give a double doublet (δ 3.64, *J* = 13.3 and 7.0 Hz), the protons of the allylic =CH_2 group at a double bond appear as coupled double doublets (δ 5.13, *J* = 17.1 and 2.0 Hz; δ 4.79, *J* = 10.0 and 2.0 Hz), the methine proton of CH_2CHCH_2 fragment — as a complex signal (doublet of triplet of doublets) with three couplings (δ 5.62, *J* = 17.1, 7.0 and 10.0 Hz). The proton bonded to N atom produces a singlet at δ 4.29.

The lacking of a half of signals in the ^{1}H NMR spectrum of **9** is attributable to their strong broadening resultant from a hindered rotation of the aniline fragment about N(1)—C(1) bond. The detailed examination of the ^{1}H NMR spectrum reveals an upward baseline drift at δ 4.5—2.5 and especially at δ 2.0—0.0. As the C(1)—N(1) and N(1)—$C(16)_{ipso}$ bonds are single and N(1) atom, in contrast with the amido nitrogen N(1) in complex **8**, does not close a chelate ring, there is a possibility for the inversion of its pyramidal geometry.

Crystal structure of complex **9** was determined from X-ray diffraction analysis and is shown in Figure 6.

The unit cell of amino-imine **9** incorporates four pairs of nonequivalent molecules. The key difference is in the attachment mode of the allyl group on a five-membered ring: it is oriented either towards the geometrical center of the naphthalene moiety (and thus configured over the acenaphthene plane) or outward from this centroid and away from the amino-imine. Bond lengths in all molecules differ inconsiderably, so we will discuss the data of one molecule. Nonsymmetry of the structure **9** (see Fig. 6) is evident in different C—N bond lengths. The C(2)—N(2) (1.272(1) Å) is a double bond and is substantially shorter compared to a single C(1)—N(1) bond (1.489(2) Å). The N(1) nitrogen in **9** has the trigonal-pyramidal coordination. In contrast to complexes **5** and **6**, compound **9** crystallizes to produce a unit cell containing both *R* and *S* isomers.

In summary, we have synthesized and characterized four novel chiral amido-imine complexes of aluminum, gallium, and indium (compounds **4**—**6** and **8**). The reaction between Group 13 metal alkyls and diimine **1** was demonstrated to lead to a single product of 1,2-addition to the ligand C=N double bond regardless of the initial reactant ratio. As indicated by X-ray diffraction data, gallium and indium chiral amido-imine complexes (**5** and **6**, respectively) unlike analogous complexes of zinc and magnesium, crystallize as a conglomerate (mechanical mixture of enantiomers).

Experimental

All the compounds mentioned above except **1** and **9** are air- and moisture-sensitive, thus all manipulations on their synthesis, isolation and identification were performed *in vacuo* using standard Schlenk techniques. Diimine dpp-BIAN was obtained *via* condensation of acenaphthenequinone with 2,6-diisopropylaniline in acetonitrile by the known procedure.[13] The compound dpp-BIANAlI(Et_2O) was synthesized as described previously.[14] Melting points were determined in vacuum-sealed capillary tubes. Diethyl ether, hexane, and toluene were dried and stored over sodium/benzophenone, and withdrawn by vacuum condensation immediately before use. IR spectra were measured from compound suspensions in the Vaseline oil on a FSM-1201 spectrometer. ^1H and ^{13}C NMR spectra were recorded on Bruker ARX 200, Bruker DPX 200, and Bruker ARX 400 spectrometers.

[(2,6-Diisopropylphenyl){2-(2,6-diisopropylphenylimino)-1-isobutyl-1,2-dihydroacenaphthylen-1-yl}amino]diisobutylaluminum (4). To the solution of dpp-BIAN (0.50 g, 1.0 mmol) in toluene (40 mL) was added Bu^i_3Al (0.20 g, 1.0 mmol). On addtion the solution changed color from a yellow to brown. The solution was heated for 1 h at 90 °C. Then toluene was replaced by hexane. Hexane solution was concentrated to yield compound **4** as red crystals (0.64 g, 92%), m.p. 162 °C. Found (%): C, 82.45; H, 9.63. $C_{48}H_{67}AlN_2$ (M = 699.05 g mol^{-1}). Calculated (%): C, 82.47; H, 9.66. IR, ν/cm^{-1}: 1613 w, 1591 m, 1545 w, 1512 m, 1315 s, 1255 m, 1209 w, 1134 w, 1110 w, 1001 m, 927 m, 809 m, 764 s, 730 m, 687 m, 561 m, 427 w. ^1H NMR (200 MHz, C_6D_6, 20 °C, for a—g labeling of functional groups see Fig. 3), δ: 7.48 (dd, 1 H, naphthalene moiety, J = 7.5 Hz, J = 1.8 Hz);7.45—7.25 (m, 6 H, 2 $C_6\underline{H}_3Pr^i{}_2$); 7.12 (dd, 1 H, naphthalene moiety, J = 7.5 Hz, J = 1.8 Hz); 6.96 (dd, 1 H, naphthalene moiety, J = = 7.0 Hz, J = 8.0 Hz); 6.80 (dd, 1 H, naphthalene moiety, J = 7.3 Hz, J = 8.0 Hz); 6.48 (d, 1 H, naphthalene moiety, J = = 7.3 Hz); 6.32 (d, 1 H, naphthalene moiety, J = 7.0 Hz); 4.90 (sept, 1 H, a-group $C\underline{H}Me_2$, J = 6.8 Hz); 3.64 (sept, 1 H, b-group $C\underline{H}Me_2$, J = 6.8 Hz); 3.38 (sept, 1 H, c-group $C\underline{H}Me_2$, J = 6.8 Hz); 3.29 (d, 1 H, g-group $C\underline{H}_aH_bCH_cMe_2$, J = 13.6 Hz); 3.07 (sept, 1 H, d-group $C\underline{H}Me_2$, J = 6.8 Hz); 2.65 (dd, 1 H, g-group $CH_a\underline{H}_bCH_cMe_2$, J = 13.6 Hz, J = 8.8 Hz); 2.55 (m, 1 H, e-group $AlCH_2C\underline{H}Me_2$, J = 6.6 Hz, J = 6.5 Hz, J = 6.3 Hz); 2.26 (sept, 1 H, f-group $AlCH_2C\underline{H}Me_2$, J = 7.0 Hz, J = 6.6 Hz); 1.71 (d, 3 H, a-group $CH(C\underline{H}_3)Me$, J = 6.8 Hz); 1.66 (d, 3 H, a-group $CH(Me)(C\underline{H}_3)$, J = 6.8 Hz); 1.59 (d, 3 H, b-group $CH(C\underline{H}_3)(Me)$, J = 6.8 Hz); 1.49 (d, 3 H, e-group $AlCH_2CH(C\underline{H}_3)(Me)$, J = 6.3 Hz); 1.43 (d, 3 H, c-group $CH(C\underline{H}_3)(Me)$, J = 6.8 Hz); 1.38 (d, 3 H, e-group $AlCH_2CH(Me)(C\underline{H}_3)$, J = 6.6 Hz); 1.28 (d, 3 H, d-group $AlCH_2CH(C\underline{H}_3)(Me)$, J = 6.6 Hz); 1.25 (d, 3 H, c-group $CH(Me)(C\underline{H}_3)$, J = 6.8 Hz); 1.13 (d, 3 H, f-group $AlCH_2CH(C\underline{H}_3)(Me)$, J = 6.6 Hz); 1.06—0.82 (м, 6 H, g-group $CH_aH_bC\underline{H}_c(Me)_2$, g-group $CH_aH_bCH_c(C\underline{H}_3)(Me)$, e-group $AlC\underline{H}_2CH(Me)(Me)$); 0.94 (d, 3 H, f-group $AlCH_2CH(Me)(C\underline{H}_3)$, J = 6.6 Hz); 0.62 (d, 3 H, c-group $CH(Me)(C\underline{H}_3)$, J = 6.8 Hz); 0.45 (d, 2 H, f-group $AlC\underline{H}_2CH(Me)(Me)$, J = 7.0 Hz); –0.04 (d, 3 H, d-group $CH(Me)(C\underline{H}_3)$, J = 6.8 Hz); –0.37 (d, 3 H, g-group $CH_aH_bCH_c(Me)(C\underline{H}_3)$, J = 5.8 Hz).

[(2,6-Diisopropylphenyl){2-(2,6-diisopropylphenylimino)-1-ethyl-1,2-dihydroacenaphthylen-1-yl}amino]diethylgallium (5). To the solution of dpp-BIAN (0.50 g, 1.0 mmol) in toluene (40 mL) was added Et_3Ga (0.16 g, 1.0 mmol). The reaction mixture was heated for 1 h at 90 °C. On heating the solution changed color from a yellow to red-brown. Then toluene was replaced by hexane. Crystallization from hexane yielded compound **5** as red-brown crystals (0.57 g, 87%). M.p. 173 °C. IR, ν/cm^{-1}: 1937 w, 1901 w, 1872 w, 1843 w, 1807 w, 1783 w, 1709 w, 1687 w, 1626 s, 1587 s, 1535 w, 1490 m, 1365 s, 1308 s, 1287 m, 1253 s, 1204 s, 1189 s, 1167 s, 1136 m, 1102 s, 1078 m, 1046 s, 1021 s, 1005 s, 969 m, 956 m, 937 s, 924 m, 905 w, 880 m, 860 m, 835 m, 822 w, 803 s, 783 s, 762 s, 752 s, 700 w, 647 m, 633 m, 611 m, 595 m, 579 m, 537 s, 513 m, 500 m, 467 m, 450 m, 422 m. ^1H NMR (400 MHz, THF-d_8, 20 °C, a—g labeling of functional groups is as shown in Fig. 3 for complex **4**), δ: 8.03 (d, 1 H, naphthalene moiety, J = 8.3 Hz); 8.01 (d, 1 H, naphthalene moiety, J = 8.3 Hz); 7.50—7.45 (м, 3 H, $C_6\underline{H}_3Pr^i{}_2$); 7.39 (dd, 1 H, naphthalene moiety, J = 7.3 Hz, J = 8.3 Hz); 7.32 (dd, 1 H, naphthalene moiety, J = 7.3 Hz, J = 8.3 Hz); 7.21 (dd, 1 H, $C_6\underline{H}_3Pr^i{}_2$, J = 7.5 Hz, J = 1.5 Hz); 7.05 (dd, 1 H, $C_6\underline{H}_3Pr^i{}_2$, J = 7.5, J = 7.8); 6.84 (dd, 1 H, $C_6\underline{H}_3Pr^i{}_2$, J = 7.8 Hz, J = 1.5 Hz); 6.40 (d, 1 H, naphthalene moiety, J = 7.3 Hz); 6.15 (d, 1 H, naphthalene moiety, J = 7.3 Hz); 4.58 (sept, 1 H, a-group $C\underline{H}Me_2$, J = 7.0 Hz); 3.43 (sept, 1 H, b-group $C\underline{H}Me_2$, J = 6.8 Hz); 3.13 (sept, 1 H, c-group $C\underline{H}Me_2$, J = 6.8 Hz); 2.84 (sept, 1 H, d-group $C\underline{H}Me_2$, J = 6.8 Hz); 2.73 (м, 1 H, e-group $C\underline{H}_aH_bMe$); 2.41 (m, 1 H, g-group $CH_a\underline{H}_bMe$); 1.45 (d, 3 H, a-group $CH(C\underline{H}_3)(Me)$, J = 7.0 Hz); 1.43 (d, 3 H, b-group $CH(C\underline{H}_3)(Me)$, J = 6.8 Hz); 1.33 (t, 3 H, f-group $GaCH_2C\underline{H}_3$, J = 8.0 Hz); 1.27 (d, 3 H, a-group $CH(Me)(C\underline{H}_3)$, J = 7.0 Hz); 1.24 (d, 3 H, c-group $CH(C\underline{H}_3)(Me)$, J = 6.8 Hz); 1.19 (d, 3 H, b-group $CH(Me)(C\underline{H}_3)$, J = 6.8 Hz); 1.00 (м, 2 H, f-group $GaC\underline{H}_2Me$); 0.91 (d, 3 H, d-group $CH(C\underline{H}_3)(Me)$, J = 6.8 Hz); 0.88 (t, 3 H, g-group $GaCH_2C\underline{H}_3$, J = 8.0 Hz); 0.60 (d, 3 H, c-group $CH(Me)(C\underline{H}_3)$, J = 6.8 Hz); 0.47 (m, 2 H, g-group $GaC\underline{H}_2Me$); 0.11 (t, 3 H, e-group $CH_2C\underline{H}_3$, J = 7.5 Hz); –0.27 (d, 3 H, d-group $CH(Me)(C\underline{H}_3)$, J = 6.8 Hz). ^{13}C NMR (400 MHz, THF-d_8, 20 °C), δ: 191.9, 150.5, 149.1, 146.1, 141.1, 140.9, 140.7, 139.7, 131.8, 130.9, 128.7, 128.3, 127.3, 127.1, 125.1, 124.7, 124.3, 80.6, 66.9, 66.0, 40.6, 28.7, 28.1, 28.0. 27.2, 26.4, 25.6, 25.1, 24.3, 23.9, 23.7, 20.8, 10.9, 9.9, 9.6, 8.6, 3.7.

[(2,6-Diisopropylphenyl){2-(2,6-diisopropylphenylimino)-1-methyl-1,2-dihydroacenaphthylen-1-yl}amino]dimethylindium (6). To the cool solution of dpp-BIAN (0.50 g, 1.0 mmol) in toluene (30 mL) was added Me_3In (0.16 g, 1.0 mmol). The reaction mixture was heated for 1 h at 90 °C. On heating the solution changed color from a yellow to red-brown. Then toluene was replaced by hexane. Compound **6** was crystallized from hexane as red rhombs. Yield 0.55 g (83%), m.p. 202 °C. IR, ν/cm^{-1}: 1634 s, 1618 m, 1587 m, 1542 w, 1512 w, 1491 m, 1428 m, 1366 m, 1347 m, 1313 m, 1271 w, 1252 m, 1204 m, 1194 m, 1188 w, 1175 w, 1154 m, 1106 m, 1076 m, 1055 w, 1046 m, 1015 m, 991 w, 980 w, 970 w, 961 w, 936 w, 849 m, 832 m, 801 m, 785 m, 771 m, 757 m, 696 w, 677 m, 663 w, 627 w, 612 m, 596 w, 577 w, 545 m, 496 m, 481 m, 465 w, 453 w, 422 m. ^1H NMR (200 MHz, C_6D_6, 20 °C, a—g labeling of functional groups is as shown in Fig. 3 for complex **4**), δ: 7.35 (dd, 1 H, naphthalene moiety, J = 7.5 Hz, J = 1.8 Hz); 7.31—7.16 (m, 6 H, 2 $C_6\underline{H}_3Pr^i{}_2$); 7.04 (dd, 1 H, naphthalene moiety, J = 7.5 Hz, J = 1.8); 6.97 (dd, 1 H, naphthalene moiety, J = 7.0 Hz, J = 8.3 Hz); 6.79 (dd, 1 H, naphthalene moiety, J = = 7.5 Hz, J = 7.8 Hz); 6.43 (d, 2 H, naphthalene moiety, J = 7.0 Hz); 4.74 (sept, 1 H, a-group $C\underline{H}Me_2$, J = 7.0 Hz); 3.47

(sept, 1 H, b-group C$\underline{H}$Me$_2$, *J* = 6.8 Hz); 3.22 (sept, 1 H, c-group C$\underline{H}$Me$_2$, *J* = 6.5 Hz); 2.98 (sept, 1 H, d-group C$\underline{H}$Me$_2$, *J* = 6.8 Hz); 1.97 (s, 3 H, e-group Me); 1.57 (d, 3 H, a-group CH(C$\underline{H}_3$)(Me), *J* = 7.0 Hz); 1.34 (d, 3 H, a-group CH(Me)-(C$\underline{H}_3$), *J* = 7.0 Hz); 1.29 (d, 3 H, b-group CH(C$\underline{H}_3$)(Me), *J* = 6.8 Hz); 1.20 (d, 3 H, b-group CH(Me)(C$\underline{H}_3$), *J* = 6.8 Hz); 1.07 (d, 3 H, d-group CH(C$\underline{H}_3$)(Me), *J* = 6.8 Hz); 1.02 (d, 3 H, c-group CH(C$\underline{H}_3$)(Me), *J* = 6.5 Hz); 0.72 (d, 3 H, c-group CH(Me)(C$\underline{H}_3$), *J* = 6.5 Hz); 0.45 (s, 3 H, f-group InMe); –0.01 (d, 3 H, d-group CH(Me)(C$\underline{H}_3$), *J* = 6.8 Hz); –0.04 (s, 3 H, g-group InMe).

[(1-Allyl-2-(2,6-diisopropylphenylimino)-1,2-dihydroacenaphthylen-1-yl){2,6-diisopropylphenyl}amino]aluminum bromoiodide (8). Ether solution containing AlI$_3$ (0.14 g, 0.33 mmol) (or I$_2$ (0.13 g, 0.5 mmol)) and dpp-BIAN (0.50 g, 1.0 mmol) was added to fine powdered aluminum foil. Reaction mixture was stirred for 12 h until its color turned to stable rich blue. Then the solution was decantated to remove excess metal.[14] Thus formed ether solution of dpp-BIANAlI(Et$_2$O) was treated with allyl bromide (0.14 g, 1.0 mmol); on addtion it changed color from a blue to buff. The solution was concentrated to yield compound **8** (0.43 g, 55%) as orange crystals. M.p. 193 °C. Found (%): C, 60.37; H, 5.84. C$_{39}$H$_{45}$AlBrIN$_2$ (*M* = 775.58 g mol^{-1}). Calculated (%): C, 60.34; H, 5.80. ^{1}H NMR (200 MHz, C$_6$D$_6$, 20 °C), δ: 7.42—7.19 (m, 6 H, 2 C$_6\underline{H}_3$Pr$^i{}_2$ and 1 H, naphthalene moiety); 7.15 (dd, 1 H, naphthalene moiety, *J* = 7.0 Hz, *J* = = 2.0 Hz); 6.96 (dd, 1 H, naphthalene moiety, *J* = 7.0 Hz, *J* = 8.3 Hz); 6.72 (dd, 1 H, naphthalene moiety, *J* = 7.5 Hz, *J* = 7.8 Hz); 6.47 (d, 1 H, naphthalene moiety, *J* = 7.5 Hz); 6.33 (d, 1 H, naphthalene moiety, *J* = 7.0 Hz); 4.89 (sept, 1 H, a-group C$\underline{H}$Me$_2$, *J* = 7.0 Hz); 3.94 (sept, 1 H, b-group C$\underline{H}$Me$_2$, *J* = 6.5 Hz); 3.47 (sept, 1 H, c-group C$\underline{H}$Me$_2$, *J* = 6.8 Hz); 2.95 (sept, 1 H, d-group C$\underline{H}$Me$_2$, *J* = 6.8 Hz); 1.66 (d, 3 H, c-group CH(C$\underline{H}_3$)(Me), *J* = 6.8 Hz); 1.61 (d, 3 H, a-group CH(C$\underline{H}_3$)-(Me), *J* = 7.0 Hz); 1.55 (d, 3 H, c-group CH(Me)(C$\underline{H}_3$), *J* = = 6.8 Hz); 1.42 (d, 3 H, b-group CH(C$\underline{H}_3$)(Me), *J* = 6.5 Hz); 1.34 (d, 3 H, d-group CH(C$\underline{H}_3$)(Me), *J* = 6.8 Hz); 1.19 (d, 3 H, a-group CH(Me)(C$\underline{H}_3$), *J* = 7.0 Hz); 0.51 (d, 3 H, b-group CH(Me)(C$\underline{H}_3$), *J* = 6.5 Hz); 0.19 (d, 3 H, d-group CH(Me)(C$\underline{H}_3$), *J* = 6.8 Hz).

***N*,*N*´-(1-Allylacenaphthylen-1(1*H*)-yl-2(1*H*)-ilidene)bis-(2,6-diisopropylbenzenamine) (9).** To ether solution of (All—dpp-BIAN)AlBrI (synthesized *in situ* from dpp-BIAN (0.50 g, 1.0 mmol)) was added H$_2$O (0.30 mL). On addtion the solution changed color from a buff to yellow. All volatile reaction mixture components were removed *in vacuo*, then hexane (30 mL) was added. This solution was filtered and concentrated to ~15 mL. Compound **9** was further isolated as yellow crystals. Yield 0.42 g (78%), m.p. 205 °C. Found (%): C, 85.67; H, 8.64. C$_{39}$H$_{46}$N$_2$ (*M* = 542.78 g mol^{-1}). Calculated (%): C, 86.22; H, 8.47. ^{1}H NMR (200 MHz, CDCl$_3$, 20 °C), δ: 7.47—7.33 (m, 5 H, 2 C$_6\underline{H}_3$Pr$^i{}_2$); 7.29—7.14 (m, 4 H, naphthalene moiety); 6.98—6.87 (m, 2 H, naphthalene moiety); 6.74 (d, 1 H, C$_6\underline{H}_3$Pr$^i{}_2$, *J* = 7.0 Hz); 5.62 (dtd, 1 H, CH$_2$C$\underline{H}$CH$_2$, *J* = 17.1 Hz, *J* = 7.0 Hz, *J* = 10.0 Hz); 5.13 (dd, 1 H, CH$_2$CHC$\underline{H}_2$, *J* = 17.1 Hz, *J* = 2.0 Hz); 4.79 (dd, 1 H, CH$_2$CHC$\underline{H}_2$, *J* = 10.0 Hz, *J* = 2.0 Hz); 4.29 (s, 1 H, NH); 3.64 (dd, 2 H, C$\underline{H}_2$CHCH$_2$, *J* = 13.3 Hz, *J* = 7.0 Hz); 3.46 (sept, 1 H, C$\underline{H}$Me$_2$, *J* = 6.8 Hz); 3.33 (sept, 1 H, C$\underline{H}$Me$_2$, *J* = 6.8 Hz); 1.42 (d, 3 H, CH(C$\underline{H}_3$)(Me), *J* = 6.8 Hz); 1.36 (d, 3 H, CH(Me)(C$\underline{H}_3$), *J* = 6.8 Hz); 1.16 (d, 6 H, CH(C$\underline{H}_3$)(C$\underline{H}_3$), *J* = 6.8 Hz).

X-ray diffraction analysis of compounds 5, 6, and 9. Diffraction data for structures **5** and **6** were collected with a Bruker SMART APEX II CCD diffractometer (ω—φ-scans, Mo-Kα radiation, λ = 0.71072 Å, graphite monochromator) at 100 K. Diffraction data for structure **9** were collected with a Bruker AXS SMART APEX diffractometer (ω—φ-scans, Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator) at 100 K. The structures were solved by the direct method using SHELXTL program[15] and refined using the full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in idealized positions (U_{iso} = 0.08 Å^3). SADABS program[16] was used to apply absorption correction. The analysis of difference Fourier syntheses indicated that in crystal **5** one methyl group is disordered over two positions with equal occupancies. Ga—C and C—C distances in the disordered group were refined using free variables.

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