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## Introduction

Enantiomerically pure ligands are relevant for the preparation of coordination compounds which may be used as reagents or catalyzing agents in enantioselective reactions.<sup>1–4</sup> In our research program concerning enantiomerically pure metal coordination compounds,<sup>5–9</sup> we are interested in the synthesis of optically active aluminum and indium derivatives and therefore we have investigated the reactions of aluminum and indium halides with 1,4-dialkyl-1,4-diazabutadienes. These ligands have two sp<sup>2</sup> nitrogen atoms as metal coordination sites and their *N*-substituents may have stereogenic centers. 1,4-Diazabutadienes can be found in three different oxidation states: neutral, a  $\pi$  radical monoanion or a reduced dianion, Scheme 1.<sup>10,11</sup> Coordination compounds formed with the

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# 1,4-Dialkyl-1,4-diazabutadienes: their reactions with aluminum and indium halides†

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Reactions of 1,4-bis[(S) methylbenzyl]-1,4-diazabutadiene (1), 1,4-bis[(R) 1'-chlorobutan-2'-yl]-1,4-diazabutadiene (2), 1,4-bis[(S,S) 1'-chloro-1'-phenyl-propan-2'-yl]-1,4-diazabutadiene (3), and 1,4-di-*tert*-butyl-1,4-diazabutadiene (4) with aluminum and indium halides were performed. Reaction of 1,4-diazabutadienes 1–4 with two equivalents of aluminum halides in toluene afforded ionic aluminum coordination compounds (5–10) which in THF solution are transformed into 1,3-dialkyl-2-methaneiminealkyl imidazolium heterocycles (11–14) by condensation of two 1,4-diazabutadienes and elimination of amine hydrochloride. Equimolar reactions of 1–4 with InCl<sub>3</sub> in dry acetonitrile at -78 °C afforded the neutral and diamagnetic InCl<sub>3</sub> coordination compounds (15–18), which are stable in the solid state under dry conditions, but in THF solution are slowly transformed into the corresponding 1,3-dialkyl-imidazolium heterocycles 19–22. The X-ray diffraction analyses of compounds 2, 3, 10, 11, 14 and 17 are described. Quantum mechanical calculations were performed in order to find the minimum energy conformers of 1,4-diazabutadienes, 1,3-dialkyl-2-methaneiminealkyl imidazolium and 1,3-dialkyl-imidazolium derivatives as well as the aluminum and indium coordination compounds.



Scheme 1 Neutral, anion and dianionic oxidation states of 1,4-diazabutadienes.

radical anion or the dianion have been widely explored. Reactions of group 13 elements in the low oxidation state give paramagnetic products.<sup>12–17</sup> The synthesis of coordination compounds could be complicated by competition between addition and coupling processes.<sup>18</sup> The coordination chemistry of neutral diazabutadienes is less known, reactions give diamagnetic ionic coordination derivatives,<sup>19</sup> as was described for the reaction of di-*tert*-butyl-diazabutadiene with GaCl<sub>3</sub>.<sup>20</sup>

Herein, we described the reactions of aluminum and indium halides with 1,4-bis[(S) methylbenzyl]-1,4-diazabutadiene (1), 1,4-bis[(R) 1'-chlorobutan-2'-yl]-1,4-diazabutadiene (2), 1,4-bis[(S,S) 1'-chloro-1'-phenylpropan-2'-yl]-1,4-diazabutadiene (3) and 1,4-di-*tert*-butyl-1,4-diazabutadiene (4). Ligands 1–3 have tertiary *N*-substituents whereas those of 4 are quaternary, Scheme 2. Compounds 1–3 have phenyl groups and/or chlorine atoms which could give rise to intra- and intermolecular weak

<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: X-ray diffraction analysis of (*R*)-1-chloro-butan-2-amine hydrochloride (S1). Macromolecular helix arrangement in the crystal of compound 2 (S2). Theoretical conformational analysis of 1,4-dialkyl-1,4-diazabutadienes **1–4** (S3). Anagostic interactions H ··· Al found in the X-ray diffraction analysis of compound **10** (S4). Cell packing representation of compound **14** with [I<sub>3</sub>]<sup>−</sup> as the anion. (S5) Optimized conformers of compounds: **5**, **17**, **18**, **20–22** (S6). Representation of the electrostatic potentials of the indium compounds **16–18** and of the ligand **3** coordinated to one and two InCl<sub>3</sub> molecules (S7). CCDC 960655–960662. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3nj01226c



Scheme 2 1,4-Dialkyl-1,4-diazabutadiene compounds 1-4.

interactions promoting crystallization or supramolecular arrangements of their derivatives. The chloro substituents could be used to add other coordinating functional groups, such as phosphines.<sup>21</sup> It is known that diazabutadiene **4** is able to stabilize metallic derivatives because of the steric hindrance that inhibits subsequent reactions once the coordination compound is formed.<sup>22,23</sup>

# Results and discussion

#### Synthesis and structures of 1,4-diazabutadienes 1-4

Diazabutadienes **1** and **4** were prepared by reactions of aqueous glyoxal with two equivalents of the primary amines: (*S*)-methylbenzylamine and *tert*-butylamine. Compound **2** was prepared in two steps. First, (*R*)-2-amino-butan-1-ol was chlorinated with SOCl<sub>2</sub> in THF to give the (*R*)-1-chloro-butan-2-amine hydrochloride, which

in turn reacted with aqueous glyoxal and Na<sub>2</sub>CO<sub>3</sub>. It was crystallized from CHCl<sub>3</sub> and the X-ray diffraction structure was obtained. Compound **3** was synthesized by the condensation reaction of (1*S*,2*S*)-1-chloro-1-phenyl-propan-2-amine hydrochloride<sup>24</sup> with aqueous glyoxal and Na<sub>2</sub>CO<sub>3</sub>, Scheme 3. 1,4-dialkyl-1,4-diazabutadiene **1** is a liquid, whereas **2–4** are crystalline solids.

Compounds 2 and 3 are new. Their X-ray diffraction analyses were performed. They have in common a planar arrangement for the CH–N==CH–CH==N–CH chain in *trans* conformation and imines in *E* configuration. Selected bond lengths and angles are in Tables 1 and 2. The C3 substituents are perpendicular to the diazabutadiene plane with the chlorine atoms pointing to the same side.

In compound 2, six  $CH \cdots N$  and two  $CH \cdots Cl$  hydrogen bonds, together with two contacts of chlorine atoms with the

1 R = (S) CH(Me)Ph H₂O 2 R = (R) CH(Et)CH<sub>2</sub>Cl R = (S) MeBn 3 R = (S,S) CH(Me)CH(Ph)CI R = tBu4 R = tBu Ŕ 1) Na<sub>2</sub>CO<sub>3</sub>, EtOH/CH<sub>2</sub>Cl<sub>2</sub> OH. SOCI2, THF ŃH₃CI (R) R'= H, R''= Et (R) R'= H, R''= Et (1R,2S) R'= Ph, R"= Me (1S,2S) R'= Ph, R"= Me

Table 1Selected bond lengths and angles for 1,4-diazabutadiene2(S)



 Table 2
 Selected bond lengths and angles for 1,4-diazabutadiene 3(S,S)



nitrogen  $\pi$  electrons (3.17 Å;  $\Sigma_{vdWr}$  Cl–N = 3.42 Å<sup>25–27</sup>) stabilize the conformation. In the crystal, the molecules of 2 are arranged in a helix, with a path of four molecules.

In compound **3**, the phenyl groups are parallel to the diazabutadiene plane. The chlorine atoms have short distances to the nitrogen atoms (3.08 and 3.09 Å). The  $C_i$ -C5-C3 and  $C_i$ -C7-C4 angles are wide (115.0 and 114.2°) indicating repulsion between methyl and phenyl groups. One of the chlorine atoms has a C-H···Cl hydrogen bond and a Cl··· $\pi$ -interaction with another molecule, Fig. 1.

It was found in the solid state and in solution that the more stable conformation of 1,4-diazabutadienes is the *s*-*trans E,E*. The bidentate coordination of these ligands needs rotation of C2–C2' in order to get the *s*-*cis E,E* conformation. The energy barrier for this isomerization in compounds **1–4** was calculated using a quantum mechanical approach,<sup>28</sup>  $\Delta G^* = 37.0$  kJ mol<sup>-1</sup>. The energy difference between the more stable *trans* isomers and the *cis* isomers was also calculated. The values were: **1** (27.1 kJ mol<sup>-1</sup>), **2** (24.4 kJ mol<sup>-1</sup>), **3** (25.6 kJ mol<sup>-1</sup>) and **4** (30.4 kJ mol<sup>-1</sup>). The energy difference is related to the steric effects of the tertiary or quaternary substituents.

# Reactions of diazabutadienes 1-4 with aluminum halides in toluene

Reactions of 1,4-diazabutadienes 1–4 with two equivalents of aluminum halides at -78 °C in toluene and in a N<sub>2</sub> atmosphere gave the corresponding ionic aluminum coordination compounds 5–10, Scheme 4. Aluminum compounds were mainly characterized by <sup>27</sup>Al NMR, Table 3. Each spectrum presented two resonances: broad signals for the cations and sharp resonances for the anions. Compounds 5–7 are brown solids which precipitate from the reaction mixture. In THF solution, they are transformed into imidazole derivatives as will be later discussed. *N-tert*-Butyl derivatives 8–10 are more stable than 5–7, they were isolated as yellow solids. The X-ray diffraction analysis of compound 10 was conducted.

<sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds **5** and **8–10** were obtained. Comparison with data of the starting diazabutadienes shows that the C2–H protons in the coordination compounds are shifted to higher frequencies: **5** ( $\Delta\delta$  0.26 ppm); **8** ( $\Delta\delta$  1.26 ppm),



Fig. 1 Intermolecular contacts in the enantiomerically pure compound 3 (S,S).



Scheme 4 Ionic aluminum coordination compounds 5-10.

Table 3	<sup>27</sup> AL NMF	$\delta$ data [ $\delta$	mag	and	$(\Delta_{1/2},$	Hz)	of	compounds	5-10
					· · · · · · · · · · · · · · · · · · ·	· · — /			

	5	6	7	8	9	10
$ \begin{bmatrix} AlXY \end{bmatrix}^+ \\ \begin{bmatrix} AlX_3Y \end{bmatrix}^- $	+34 (1250)	+62 (3036)	+68 (3754)	+97 (3550)	+89 (2050)	+130 (2000)
	+107.1 (94)	+100.1 (40)	+100.2 (80)	+102.0 (154)	+20.0 (137)	+102.0 (22)

**9** ( $\Delta\delta$  1.49 ppm), **10** ( $\Delta\delta$  1.20 ppm), whereas the C2 signals appear at lower frequencies with respect to those of the diazabutadienes, the explanation could be based on the change of the ligand conformation from *trans* to *cis*.

The ionic coordination compound **10** crystallized from  $CHCl_3$  and the X-ray diffraction analysis was performed, selected bond lengths and angles are in Table 4. The aluminum atom is bound to the nitrogen atoms, to a chlorine atom and to a methyl group, the  $[AlCl_3Me]^-$  anion neutralizes the cation.

The *tert*-butyl protons have a short distance to the aluminum atom giving rise to anagostic interactions (2.78 and 2.99 Å,  $\Sigma_{\rm vdWr} = 3.3$  Å<sup>29</sup>). The exocyclic N–C bonds of the *tert*-butyl groups present alternate conformations with respect to the ring

Table 4 Selected bond lengths and angles for the coordination compound  ${\bf 10}$ 



Bond lengths		Bond angles	
Al1-N1	1.956(5)	N1-Al1-N2	84.6(2)
Al1-N2	1.971(5)	C5-Al1-Cl1	121.7(2)
N1-C1	1.284(7)	C1-N1-Al1	110.1(4)
N2-C2	1.279(8)	C2-N2-Al1	110.2(4)
C1-C2	1.459(9)	N1-C1-C2	117.9(5)
Al1-C5	1.971(5)	N2-C2-C1	117.1(6)
Cl1-Al1	2.077(3)	C1-N1-C3	121.3(5)
N1-C3	1.508(7)	C2-N2-C4	121.7(5)
N2-C4	1.507(8)		



**Fig. 2** Intermolecular interactions in the crystal of compound **10**. The aluminum compounds form chains by Cl···C=C  $\pi$  contacts (Cl···C distances are in the range of 3.17–3.27 Å;  $\Sigma_{vdWr}$  3.55 Å<sup>28</sup>).

plane. Each ring has two intermolecular  $Cl \cdots \pi$  interactions, Fig. 2.<sup>25–27</sup>

Due to the fact that we were unable to get crystals for compounds **6** and **7** we decided to calculate their structures in order to get some information about the possible weak interactions of the substituent chlorine atoms. The minimum energy conformers for the aluminum cations in compounds **6** and **7** were calculated,<sup>28</sup> Fig. 3. The optimized conformer of compound **6** shows that a short contact of a chlorine atom with the aluminum (2.93 Å) atom and an H···Cl intramolecular hydrogen bond stabilize the structure. A short C-H···Al distance (2.85 Å) was also found. In the calculated structure of compound **7**, the chlorine atoms are oriented towards the C==N bonds with short distances (3.08 and 3.12 Å;  $\Sigma_{vdWr} = 3.55$  Å). The methyl protons have short distances to the aluminum atom (3.08 Å).

# Reactions of 1,4-diazabutadienes 1-4 with aluminum halides in THF

Equimolar reactions of diazabutadienes 1–4 with AlX<sub>3</sub> (X = Cl, I) in dry THF at -78 °C for 2 h were performed. Examination of the reaction mixtures by <sup>27</sup>Al NMR in THF showed the presence of aluminates [AlCl<sub>4</sub>]<sup>-</sup> ( $\delta^{27}$ Al +101.3,  $\Delta_{1/2}$  215 Hz) or [AlI<sub>4</sub>]<sup>-</sup> ( $\delta^{27}$ Al –20.2,  $\Delta_{1/2}$  137 Hz). Reactions performed with AlI<sub>3</sub> in the presence of CH<sub>2</sub>Cl<sub>2</sub> afforded the corresponding [AlCl<sub>4</sub>]<sup>-</sup> anions.



Fig. 3 Calculated minimum energy structures for cations 6 and 7.



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Scheme 5 Transformation of compounds 5-8 into 11-14.

Solvent extraction of the reaction products and water washing gave the heterocycles stabilized by chloride anions. Compounds 11, 13 and 14 are brown solids, whereas 12 is a viscous liquid. Compounds were characterized by IR, mass spectrometry and elemental analyses. The <sup>1</sup>H and <sup>13</sup>C NMR spectra indicate the formation of 1,3-dialkyl-2-methaneiminealkyl imidazolium heterocycles 11-14, Scheme 5. To our knowledge the aluminum compounds' transformation into the imidazolium heterocycles has not been described before. The new compounds show an imine group attached to C2, as a result of the condensation of one diazabutadiene with half of another diazabutadiene. 1,3-Dialkyl-2-methaneiminealkyl imidazoliums (11-14) are analogues of  $\alpha$ , $\beta$ -unsaturated acyl imidazolium cations, intermediates in polymer syntheses.<sup>30</sup> They are also structurally related to imidazolium 2-carboxylates used as pre-catalysts for polyurethane formation.<sup>31</sup>

A possible reaction path for the synthesis of 1,3-dialkyl-2methaneiminealkyl imidazolium compounds under anhydrous conditions and in HCl was proposed earlier.<sup>32</sup> A similar path can be depicted for the  $AlCl_3$  reaction. It is assumed that the aluminum coordination compounds **5–10** could suffer a nucleophilic attack from a diazabutadiene to one of the carbon atoms of the metallacycle with elimination of  $AlCl_2NHR$ , Scheme 6.

Compound **11** crystallized from CHCl<sub>3</sub>. Selected bond lengths and angles are in Table 5. The exocyclic imine is almost coplanar with the imidazolium ring (the N–C–C–N dihedral

angle is 13°). The benzylic carbon atoms of the intracyclic nitrogen atoms are also in the imidazolium plane. The phenyl groups are pointing to the opposite sides of the ring plane. The conformation of one of the endocyclic *N*-substituents is fixed by a hydrogen bond between the benzylic proton and the exocyclic imine (2.47 Å). The other endocyclic *N*-substituent presents some disorder due to its free rotation. One of the chlorine atoms of the [AlCl<sub>4</sub>]<sup>-</sup> anion has a Cl···C  $\pi$ -interaction (3.41 Å) with the imidazolium C2 (not shown).<sup>25–27</sup>

The reaction of **4** with  $AlCl_3$  afforded crystals of **14** with  $[AlCl_4]^-$  as the anion whereas the  $AlI_3$  reaction product treated with water and extracted with  $CH_2Cl_2$  afforded crystals of **14** with  $[I_3]^-$  as the anion. The two crystals were subjected to the X-ray diffraction analyses; selected bond lengths and angles are in Table 6.

The cation has the same conformation in both crystals. The plane of the exocyclic imine is perpendicular to the imidazolium ring, Fig. 4A. This conformation is different from that of **11**, and is attributed to the steric effect. Two *tert*-butyl methyl groups have two C-H···C  $\pi$ -interactions (2.32 and 2.34 Å) with the exocyclic imine. The imidazolium ring is aromatic (bond lengths vary from 1.34 to 1.37 Å). In the crystal of **14** [AlCl<sub>4</sub>]<sup>-</sup>, one chlorine atom has a  $\pi$  contact<sup>25–27</sup> with the imidazolium C2, Fig. 4B. The X-ray diffraction structure of 1,3-di-*tert*-butyl-2-[*N*-*tert*-butylmethanimine]-imidazolium having Cl<sup>-</sup> as the anion is known. The compound was synthesized by reaction of the diazabutadiene with dry HCl in anhydrous toluene.<sup>32</sup>



Scheme 6 1,3-Dialkyl-2-methaneiminealkyl imidazolium heterocycles could be formed by the nucleophilic attack of diazabutadienes to the aluminum coordination compounds.

Table 5 Selected bond lengths and angles for the imidazolium cation 11



 Table 6
 Selected bond lengths and angles for the imidazolium cation 14



14[AlCl <sub>4</sub> ]		<b>14</b> [ <i>I</i> <sub>3</sub> ]			
Bond lengths	Bond angles	Bond lengths	Bond angles		
N1-C3         1.339(6)           N2-C3         1.333(6)           N1-C1         1.391(6)           N2-C2         1.372(6)           C2-C1         1.315(7)           C3-C4         1.482(7)           N3-C4         1.240(6)           N1-C5         1.518(6)           N2-C6         1.522(6)           N3-C7         1.50(2)	) N2-C3-N1 107.9(4) C3-N1-C1 108.7(4) C3-N2-C2 107.8(4) C2-C1-N1 106.1(5) C1-C2-N2 109.5(5) N3-C4-C3 119.1(5) C3-N1-C5 128.9(4) C3-N2-C6 127.2(4) C4-N3-C7 123.9(7)	) C3-N1 1.28(3) ) C3-N2 1.34(2) ) C1-N1 1.39(3) ) C2-N2 1.41(3) ) C2-C1 1.29(3) ) C3-C4 1.49(3) ) C4-N3 1.26(3) ) C5-N1 1.52(3) ) C6-N2 1.47(3) C7-N3 1.48(3)	N1-C3-N2 112(2) C3-N1-C1 107(2) C3-N2-C2 104(2) C2-C1-N1 108(2) C1-C2-N2 109(2) N3-C4-C3 121(2) C3-N1-C5 130(2) C3-N2-C6 131(2) C4-N3-C7 123(2)		

Optimization of the minimum energy conformations of 1,3-dialkyl-2-methaneiminealkyl imidazolium compounds **11–14** was performed.<sup>28</sup> The calculated structures of cations **11** and **14** are similar to their X-ray diffraction structures; therefore we have concluded that calculated cations **12** and **13** (Fig. 5) could be used to analyze their conformations and possible weak interactions. In both structures the exocyclic imines are coplanar with the imidazolium ring due to the electronic delocalization and formation of a CH···N hydrogen bond [C-H···N distances: 2.27 Å (**12**) and 2.17 Å (**13**)]. The *N*-tertiary carbon reduces the steric effect and allows formation of a stabilizing hydrogen bond. In cations **12** and **13** some chlorine atoms are oriented towards the  $\pi$  electrons of the ring nitrogen atoms (**12** 3.15 Å; **13** 3.05 Å).

In order to know the contribution of the exocyclic imine to the stabilization of the molecule, we have calculated the energy of two conformers for the hypothetical molecule 1,3-di(methyl)-2-[*N*-methylmethanimine]-imidazolium, where the steric effect has been minimized. We have found that the coplanar conformation of the exocyclic imine is more stable than the perpendicular conformation by 13.6 kJ mol<sup>-1</sup>, Fig. 6.

#### Reactions of 1,4-diazabutadienes 1-4 with InCl<sub>3</sub> in acetonitrile

Reactions of compounds 1–4 with one or two equivalents of  $InCl_3$  in dry acetonitrile and a  $N_2$  atmosphere at -78 °C gave the indium coordination compounds 15–18, Scheme 7. Neutral and diamagnetic indium coordination compounds derived from 1,4-diazabutadienes are not described in the literature.



Fig. 4 X-Ray diffraction structure of imidazolium **14**. (A) The cation has four hydrogen bonds to the exocyclic C=N bond (2.37–2.95 Å). (B) One chlorine atom of the anion has a Cl $\cdots$ C2  $\pi$ -interaction.



Fig. 6 Calculated minimum energy conformers for 1,3-dimethyl-2-[N-methylmethanimine]-imidazolium.



Compounds are stable in the solid state under dry conditions. In the IR spectra the C—N bands of the starting diazabutadienes (1633 cm<sup>-1</sup>) become broad and are shifted towards lower frequencies (1605 cm<sup>-1</sup>). In the NMR spectra, the C2–H protons signals are shifted to the higher frequencies with respect to the starting diazabutadienes, whereas the chemical shifts of C2 are shielded (between 2–4 ppm) probably due to the diazabutadiene conformational change. A similar behavior was found for the aluminum compounds **5**, **8–10**.

В

We have followed the reactions of compound 3 with one and two equivalents of InCl<sub>3</sub> in THF by <sup>1</sup>H and <sup>13</sup>C NMR at low temperature. The spectra of the reaction of 3 with one equivalent of InCl<sub>3</sub> in TDF at -65 °C show at least five compounds out of which one was predominant [<sup>1</sup>H: 8.9 (H1), 5.9 (H4), 4.4 (H3), 1.3 (H5) ppm; <sup>13</sup>C: 158.7 (C1), 138.7 (C<sub>i</sub>), 75.9 (C4) and 19.0 (C5) ppm]. All signals were very broad, indicating isomers in equilibrium. When the solution was heated at +20 °C, only one set of broad





signals was observed [<sup>1</sup>H: 8.0 (H2), 5.0 (H4), 3.7 (H3), 1.0 (H5) ppm; <sup>13</sup>C: 161.7 (C2), 139.1 (C<sub>*i*</sub>), 71.9 (C4), 65.0 (C3) and 19.0 (C5) ppm], which reveals that isomers are in fast equilibrium and that their signals were averaged, Scheme 8. It is assumed that the indium is coordinated by nitrogen and chlorine atoms because, all carbon and hydrogen atoms showed broad signals, Scheme 9.

The reaction of 3 with two equivalents of  $InCl_3$  in TDF at -65 °C showed seven sets of broad signals attributed to isomers of coordination compounds. When the solution reached +20 °C, only two sets of broad signals were observed, indicating the existence of fast equilibrium between the isomeric species. One of the signal sets corresponds to that observed in the spectrum of the equimolar reaction (~35%). Whereas, the second set [<sup>1</sup>H: 7.8 (H2), 5.6 (H4), 4.4 (C3) and 1.3 (5) ppm; <sup>13</sup>C: 159.1 (C2),

138.6 (C<sub>i</sub>), 71.9 (C4), 66.0 (C3) and 18.5 (C5) ppm] was attributed to the complex of the 1,4-diazabutadiene with two molecules of InCl<sub>3</sub> (~65%), Scheme 9. Calculation of the optimized structure is shown in Fig. 7. The In…Cl distances (3.61 Å,  $\Sigma_{vdWr} = 4.0 Å^{29}$ ) indicate that the C–Cl chlorine atoms have stabilizing contacts with the indium atom. A similar fluxional behavior was found for a platinum derivative of ligand 4.<sup>33</sup>

From the reaction of diazabutadiene 3 with  $InCl_3$ , a solid was obtained which was dissolved in THF and crystals of compound 17 suitable for X-ray diffraction analyses were obtained. Selected bond lengths and angles are in Table 7.

It was found that the indium atom is hexacoordinated with an octahedral geometry. It is chelated by the diazabutadiene and coordinated to three chlorine atoms and to one THF molecule. The THF is located perpendicular to the metallacycle plane. The C–Cl atoms are in opposite faces of the ring with short distances to the nitrogen atoms (3.06 and 3.15 Å). The coordinated oxygen atom has a planar geometry attributed to sp<sup>2</sup> hybridization. The chlorine atoms situated in the metallacycle plane have hydrogen bonds with the methyl and benzylic groups Cl4 $\cdots$ H–C19 (2.643 Å), Cl5 $\cdots$ H–C6 (2.641 Å). Intermolecular interactions are depicted in Fig. 8.

To our knowledge there is only another X-ray diffraction analysis reported for an indium compound where the metal atom is coordinated to a 1,4-diazabutadiene.<sup>15</sup> It is a paramagnetic compound of formula LInCl<sub>2</sub>·THF (L = 1,4-diisopropylphenyl-1,4-diazabutadiene), in the reported compound the indium is



Fig. 7 Calculated minimum energy structure for diazabutadiene 3 coordinated to two InCl<sub>3</sub>.

Table 7 Selected bond lengths and angles for compound 17



Bond lengths	5	Bond angles	Bond angles		
In-N1	2.313(7)	N1-In-N2	72.2(2)		
In-N2	2.380(6)	Cl4-In-Cl5	95.06(8)		
N1-C1	1.242(9)	Cl3-In-O1	172.4(2)		
N2-C2	1.26(1)	N1-In-Cl4	98.3(2)		
C1-C2	1.50(1)	N2-In-Cl5	93.6(2)		
N1-C3	1.453(9)	C1-N1-In1	114.8(6)		
N2-C4	1.492(9)	C2-N2-In1	112.1(5)		
Cl1-C5	1.817(9)	C1-N1-C3	116.3(7)		
Cl2-C7	1.825(9)	C2-N2-C4	117.9(7)		
In-Cl3	2.438(2)	C3-C5-Cl1	106.9(6)		
In-Cl4	2.434(2)	C4-C7-Cl2	108.7(7)		
In–Cl5	2.427(2)				
In-O1	2.287(6)				



**Fig. 8** The indium coordination compound **17** forms chains by cooperative C-H···Cl hydrogen bonds (Cl3···H-C3 2.762 Å, Cl4···H-C3 2.865 Å) and Cl5··· $\pi$ -interactions [Cl5···C3 (3.35 Å); Cl5···C4 (3.24 Å)].

pentacoordinated, the THF is in the *anti* position to one nitrogen atom and the ligand is a radical monoanion.

The optimized conformation for compound **17** is similar to its X-ray diffraction analysis structure; therefore calculations could provide a good approach for determining the structure of coordinated indium compounds that could not be crystallized. The calculated minimum energy conformer<sup>29</sup> for compound **16** coordinated to THF is shown in Fig. 9. The chlorine atoms in the structure are oriented towards the imine  $\pi$  electrons.

#### Reactions of diazabutadienes 1-4 with InCl<sub>3</sub> in THF

The reactions of ligands 1-4 with  $InCl_3$  in THF at room temperature were followed by NMR. The formation of the





indium coordination compounds was observed, and then the signals for the 1,3-dialkyl-imidazolium tetrachloroindates **19–22** slowly emerged, Scheme 10. The transformations attained after one week were 21% for **19**; 98% for **20**, 25% for **21** and 25% for **22**. It was observed that these reactions slowed down in the dark; therefore they could be photo-induced.<sup>34</sup>

The transformation of the ionic indium coordination compound into the imidazoliums **19–21** is interesting because the only evident source for the carbon introduced into the imidazole ring was the ligand itself. Therefore it is assumed that the C–H imidazolium compounds may come from the **1**,3-dialkyl-2-methaneiminealkyl imidazolium derivatives (**11–14**), which in the presence of InCl<sub>3</sub> are transformed into the relatively stable carbene-InCl<sub>3</sub>.<sup>35–37</sup> The latter by reaction with labile protons affords the C–H derivatives, Scheme **11**.

In order to check the latter statement, we have isolated the chloride of the 1,3-dialkyl-2-methaneiminealkyl imidazolium **12**, dissolved it in CH<sub>2</sub>Cl<sub>2</sub> and added one equivalent of InCl<sub>3</sub>, afterwards the reaction was followed by <sup>1</sup>H and <sup>13</sup>C NMR. Two weeks later compound **12** was transformed into compound **20** (60%). An inverse reaction is known for the alkylation of an imidazole carbene by an  $\alpha$ , $\beta$ -unsaturated enol ester.<sup>38</sup> The observation of these transformations is relevant because 1,3-dialkyl-imidazolium compounds are precursors of imidazole carbenes; important ligands for metal derivatives<sup>39</sup> also used as reagents<sup>40</sup> and as ionic liquids.<sup>41</sup> Optically active carbenes are catalyzing agents for enantiosynthesis.<sup>42,43</sup>

The structure of compounds **19–22** was determined by NMR. The aromatic character of the ring is denoted by the <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts. C1–H protons for **19–22** appear in the range of 8.3–10.63 ppm which indicates its positive character, whereas C2–H is observed at 7.14–8.08 ppm. <sup>13</sup>C NMR C1 signals are found at 130.2–138.4 ppm and C2 appears between at 120.7 and 122.4 ppm. The 1,3-dialkyl-imidazoliums **19–22** were observed in the (+)TOF mass spectra and the  $[InCl_4]^-$  anion in the (–)TOF spectra.

Calculations of the minimum energy structures of 1,3dialkylimidazolium heterocycles show that there is no steric effect between the ring and the *N*-substituents, which freely rotate.<sup>28</sup> The rotational barrier for the *t*-butyl group rotamers in compound **22** was calculated to be 2.57 kJ mol<sup>-1</sup>.







Scheme 11 Plausible transformation of 1,3-dialkyl-2-methaneiminealkyl imidazolium into the 1,3-dialkyl-imidazolium, promoted by InCl<sub>3</sub> through an intermediate carbene which is protonated.

## Conclusions

Two new 1,4-dialkyl-1,4-diazabutadienes bearing two optically active N-substituents: 1-chlorobutan-2-yl (2) and 1-chloro-1-phenyl-propan-2-yl (3) and their X-ray diffraction analyses are reported. The solid state conformation showed that the diazabutadiene system adopts the more stable *anti* conformation with imines in *E* configuration.

The reactions of diazabutadienes **1–4** with aluminum halides in toluene afforded unstable ionic coordination compounds. The X-ray diffraction of one of them was obtained. The aluminum coordination compounds in THF solution are slowly and completely transformed into **1**,3-dialkyl-2-methaneiminealkyl imidazolium heterocycles (**11–14**). This transformation has not been described before. The X-ray diffraction analysis of compounds **11** and **14** indicated that the conformation of the exocyclic imine was determined by the steric effect of the nitrogen substituents. Calculations showed that the most stable conformations were those found in the solid state.

Reactions of  $InCl_3$  with diazabutadienes 1–4 in acetonitrile afforded the corresponding neutral and diamagnetic indium coordination compounds 15–18. To our knowledge these are the first examples of diamagnetic and neutral indium coordination compounds derived from 1,4-diazabutadiene ligands. They are stable in the solid state and could be isolated. The X-ray diffraction analyses of the THF adduct of the indium coordination compound 17 was obtained.

The reactions of InCl<sub>3</sub> in THF also gave the neutral diamagnetic InCl<sub>3</sub> coordination compounds **15–18**, however in the THF solution they are slowly transformed into the **1**,3-dialkyl imidazolium heterocycles **19–21**. This transformation has not been reported before in the literature. The origin of **1**,3-dialkylimidazolium

compounds **15–18** could be explained, if it is assumed that 1,3dialkyl-2-methaneiminealkyl imidazoliums are previously formed and cleaved by the InCl<sub>3</sub> to give the corresponding carbenes stabilized by the InCl<sub>3</sub>. Consequent reactions of the carbenes with labile protons afford the C–H imidazolium heterocycles (**19–22**).

It was found that in the X-ray diffraction analyses and in calculations of compounds derived from ligands 2 and 3 that the chlorine atoms have stabilizing contacts with the  $\pi$  system of the imines.

In the reactions of  $AlCl_3$  and  $InCl_3$  with 1,4-dialkyl-1,4-diazabutadienes (1–4) the nature of the metal halides, the nitrogen substituents and the solvent determine the reaction products. The two metal coordination compounds transformations into imidazolium derivatives are of interest in the heterocyclic chemistry.

# **Experimental section**

#### General remarks

Reagents were purchased from Sigma-Aldrich Chemical, Fluka Chemika and Strem Chemical, and were not purified. Vacuum line techniques were employed for all manipulations of air and moisture sensitive compounds. THF, toluene,  $CH_2Cl_2$  and acetonitrile were dried prior to use<sup>44</sup> Dry CDCl<sub>3</sub>, DMSO-d<sub>6</sub>, THF-d<sub>8</sub>, were purchased from Aldrich and used without further purification. (1*S*,2*S*)-1-Chloro-1-phenyl-2-aminepropane hydrochloride was prepared as reported,<sup>24</sup> as well as compounds  $1^{45,46}$  and  $4.^{47}$ 

Melting points were obtained using a Mel-Temp II apparatus and are uncorrected. Mass spectra were obtained by LC/MSD TOF on an Agilent Technologies instrument with ESI as an ionization source. Elemental analyses were performed on Flash (EA) 1112 series equipment. IR spectra were recorded on a KBr disc using a FT Spectrum GX Perkin Elmer spectrometer. NMR spectra were obtained on a Jeol GSX-270, Jeol Eclipse 400 MHz and Bruker Avance 300 MHz. <sup>1</sup>H, <sup>13</sup>C, <sup>27</sup>Al [ $\Xi$  26.077, Al(NO<sub>3</sub>)<sub>3</sub>]. Numbering of atoms for identification of the NMR signals is shown in Scheme 2.

Calculations were performed in order to obtain the molecular geometries using the Gaussian  $03^{28}$  using DFT and the hybrid method B3LYPP/6-31+G(d,p). For indium compounds, the base used was 3-21G. Geometries were checked to be the minimal by the frequency analysis.

Crystallographic data were measured using a Nonius Kappa CCD instrument with a CCD area detector using graphite-monochromated MoK $\alpha$  radiation. Intensities were measured using  $\phi+\omega$  scans. Crystal data are in Tables 8 and 9. Structures were solved using direct methods with SHELX-97,  $^{48}$  Sir 2002 and Sir 2004.  $^{49}$ 

The refinement for all structures (based on  $F^2$  of all data) was performed by full matrix least-squares techniques using Crystals 12.84.<sup>50</sup> All non-hydrogen atoms were refined anisotropically. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with numbers: **2** (960655), **3**(*S,S*) (960656), **3**(*meso*) (960657), **10**(960658), **11** (960659), **14**(AlCl<sub>4</sub>)<sup>-</sup> (960660), **14**(I<sub>3</sub>)<sup>-</sup> (960661), **17** (960662), (*R*)-(-)-1-chloro-butan-2-amine hydrochloride (960663).

#### Synthesis of the compounds

(*R*)-(–)-1-Chloro-butan-2-amine hydrochloride. To a solution of (*R*)(–)-2-aminobutanol (10 g, 112 mmol) in THF (50 mL) at 0 °C, SOCl<sub>2</sub> (16.4 mL, 224 mmol) was added. The solution was stirred for 12 h at 70 °C and the resulting mixture filtered and washed with acetone. The (*R*)(–)-2-chlorobutylamine hydrochloride is a colorless solid (13.8 g, 86%), it crystallized from CHCl<sub>3</sub>. Mp. 180 °C. [ $\alpha$ ]<sub>D</sub> –9° (EtOH, 25 °C). NMR (D<sub>2</sub>O, 25 °C;  $\delta$  ppm), <sup>1</sup>H: 3.57 (qd, <sup>3</sup>J 3.46, 3.21 Hz, 1H, H4, 3.87 (dd, <sup>3</sup>J 3.46, 5.96 Hz, 2H, H3), 1.77 (qd, <sup>3</sup>J 7.42 Hz, 2H, H5), 0.99 (t, *J* 7.42 Hz, 3H, H6); <sup>13</sup>C: 53.7 (C3), 44.4 (C4), 23.3 (C5), 9.0 (C6). Anal. calcd for [C<sub>4</sub>H<sub>11</sub>Cl<sub>2</sub>N]: C, 33.52; H, 7.68; N, 9.77%; found: C, 32.84; H, 7.79; N, 9.43%.

**1,4-Bis**[(*R*)-1'-chlorobutan-2'-yl]-1,4-diazabutadiene (2). To a solution of (*R*)-(–)-1-chloro-butan-2-amine hydrochloride (5 g, 35 mmol) in EtOH/CH<sub>2</sub>Cl<sub>2</sub> [2:1] (100 mL), Na<sub>2</sub>CO<sub>3</sub> (3.71 g, 35 mmol) and then aq. glyoxal 40% (2 mL, 17.5 mmol) were slowly added and stirred for 15 h at rt. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent evaporated. Compound 2 is a yellow solid (5.8 g, 70%). Mp 56–58 °C. [ $\alpha$ ]<sub>D</sub> = + 292.45 (EtOH, 25 °C). NMR (CDCl<sub>3</sub>, 25 °C;  $\delta$  ppm), <sup>1</sup>H: 7.89 (s, 2H, H2), 3.23 (m, 2H, H3), 3.67 (dd, <sup>3</sup>J 4.35 Hz, 2H, H4a), 3.57 (dd, <sup>3</sup>J 7.70 Hz, 2H, H4b), 1.60 (qdd, <sup>3</sup>J 4.07 Hz, 2H, H5a), 1.77 (qdd, <sup>3</sup>J 4.22 Hz, 2H, H5b), 0.83 (t, <sup>3</sup>J 7.44 Hz, 6H, H6). <sup>13</sup>C:162.5 (C2), 73.6 (C3), 47.5 (C4),

 Table 8
 Crystallographic data for compounds 2, 3, 10 and 11

Compd	2	3(S,S)	10	11
Empirical formula	$C_{10}H_{18}Cl_2N_2$	$C_{20}H_{22}Cl_2N_2$	C11H23AlClN2CH3AlCl3	C <sub>28</sub> H <sub>30</sub> N <sub>3</sub> AlCl <sub>4</sub>
Formula weight	237.16	361.30	394.11	577.33
Crystal size [mm]	0.4 imes 0.2 imes 0.2	0.23 imes 0.05 imes 0.05	0.4 imes 0.15 imes 0.05	0.5 imes 0.4 imes 0.35
Crystal shape	Prism	Needle	Prism	Prism
Crystal color	Colorless	Colorless	Colorless	Colorless
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_{1}2_{1}2_{1}$	$P2_1$	Pbca	$P2_1$
a [Å]	13.2941 (5)	5.6218 (2)	11.6141 (3)	6.988 (10)
b Å	4.6884 (2)	26.6363 (11)	17.4168 (5)	23.822 (2)
c Å	21.0334 (10)	6.8310 (2)	21.0756 (8)	9.334 (5)
α[°]	90.000	90.000	90.000	90.000
β <sup>[°]</sup>	90.000	113.898 (2)	90.000	101.68
v [°]	90.000	90.000	90.000	90.000
$V[Å^3]$	1310.97	935.20 (6)	4263.2 (2)	1521 (9)
Z	4	2	8	2
$D_x$ (calcd) (mg m <sup>-3</sup> )	1.202	1.279	1.228	1.26
$\mu \left[ mm^{-1} \right]$	0.46	0.35	0.63	0.44
F(000)	504	380	1648	600
Temperature [K]	293	173	293	293
$\theta$ range for data collection	4.2-27.5	1-27.5	2.9-27.5	0.8 - 27.5
Index ranges	$-17 \leq h \leq 17$	$-7 \leq h \leq 7$	$-14 \leq h \leq 14$	$-8 \le h \le 8$
-	$-6 \leq k \leq 5$	$-20 \leq k \leq 34$	$-22 \leq k \leq 22$	$-29 \leq k \leq 30$
	$-27 \leq l \leq 27$	$-8 \leq l \leq 8$	$-27 \leq l \leq 27$	$-12 \le l \le 12$
Reflections measured	5462	6597	8869	13 617
Independent reflections	2940	2908	4677	6327
Reflections observed $[I > 2\sigma(I)]$	1788	2618	1948	4427
R(int)	0.056	0.035	0.105	0.032
Number of parameters	177	305	189	294
Weighting scheme <i>R/wR</i>	0.0497/0.1768	0.0282/0.4729	0.1191/3.1453	0.065/0.6828
GOOF	1.02	1.06	1.02	1.03
$R\left[F > 2\sigma(F^2)\right]$	0.051	0.039	0.088	0.062
$w\bar{R}(F^2)$	0.131	0.089	0.278	0.163
Largest residual peak [e Å <sup>-3</sup> ]	0.21, -0.16	0.24, -0.27	0.52, -0.39	0.42, -0.28

 $w = 1/[s^2(F_o^2) + (aP)^2 + bP]$  where  $P = (F_o^2 + 2F_c^2)/3$ .

Table 9 Crystallographic data for compounds 14 and 17

Compd	$14[AlCl_4]$	<b>14</b> [I <sub>3</sub> ]	17	Chlorohydrate
Empirical formula	C <sub>16</sub> H <sub>31</sub> N <sub>3</sub> AlCl <sub>4</sub>	$C_{16}H_{30}N_{3}I_{3}$	C <sub>24</sub> H <sub>30</sub> Cl <sub>5</sub> InN <sub>2</sub> OC <sub>4</sub> H <sub>8</sub> O	C <sub>4</sub> H <sub>11</sub> ClNCl
Formula weight	433.21	645.13	726.67	144.04
Crystal size [mm]	0.38 imes 0.3 imes 0.15	0.25 imes 0.13 imes 0.03	0.25 imes 0.05 imes 0.05	0.45 imes 0.2 imes 0.15
Crystal shape	Prism	Fragment	Needle	Prism
Crystal color	Colorless	Red	Colorless	Colorless
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Tetragonal
Space group	Pbca	$P2_{1/c}$	$P2_{1}2_{1}2_{1}$	<i>I</i> 4
a [Å]	10.9102 (3)	13.533 (2)	6.9619 (2)	14.5159 (3)
b Å	20.2966 (5)	11.4237 (13)	13.4095 (5)	14.5159 (3)
c [Å]	21.7692 (7)	18.787 (2)	35.1631 (9)	7.1671 (2)
α້ເງັ	90.000	90.000	90.000	90.000
$\beta$ [°]	90.000	125.466 (8)	90.000	90.000
v [°]	90.000	90.000	90.000	90.000
V[Å <sup>3</sup> ]	4820.6 (2)	2365.5 (5)	3282.67 (18)	1510.19 (8)
Z	8	4	4	8
$D_x$ (calcd) (mg m <sup>-3</sup> )	1.194	1.811	1.47	1.267
$\mu$ [mm <sup>-1</sup> ]	0.53	3.97	1.15	0.76
F(000)	1824	1224	1480	608.0
Temperature [K]	293	293	173	293
$\theta$ range for data collection	3.3-27.5	0.8-27.5	1.0-27.5	0.8-27.5
Index ranges	$-13 \leq h \leq 13$	$-16 \le h \le 15$	$-9 \le h \le 5$	$-18 \leq h \leq 18$
0	$-25 \le k \le 26$	$-13 \leq k \leq 14$	$-17 \leq k \leq 10$	$-18 \le k \le 17$
	$-28 \leq l \leq 28$	$-18 \leq l \leq 23$	$-45 \leq l \leq 28$	$-9 \leq l \leq 9$
Reflections measured	10 069	4431	14 201	11708
Independent reflections	5386	3093	7082	1686
Reflections observed $[I > 2\sigma(I)]$	2246	1598	3687	1490
R(int)	0.154	0.065	0.088	0.041
Number of parameters	279	209	428	108
Weighting scheme <i>R/wR</i>	0.0983/3.5245	0.1434/27.4624	0.0476	0.030/0.1586
GOOF	1.02	1.15	0.99	1.09
$R\left[F > 2\sigma(F^2)\right]$	0.088	0.109	0.071	0.026
$wR(F^2)$	0.251	0.366	0.144	0.059
Largest residual peak [e $Å^{-3}$ ]	0.38, -0.34	1.04, -1.60	0.90, -0.60	0.12, -0.16
$w = 1/[s^2(F_0^2) + (aP)^2 + bP]$ where P	$=(F_0^2+2F_c^2)/3.$			

26.5 (C5), 10.5 (C6). IR (KBr,  $\nu_{max}$  cm<sup>-1</sup>): 1625 (C=N), 729 (C-Cl). Anal. calcd for  $[C_{10}H_{18}Cl_2N_2]$ : C, 50.64; H, 7.65; N, 11.81%; found: C, 50.58; H, 8.08; N, 11.62%.

#### 1,4-Bis[(S,S)-1'-chloro-1'-phenylpropan-2'-yl]-1,4-

**diazabutadiene (3).** Compound 3 (1*S*,2*S*) was prepared from (1*R*,2*S*)-1-chloro-1-phenylpropan-2-amine hydrochloride (5 g, 24 mmol), Na<sub>2</sub>CO<sub>3</sub> (2.54 g, 24 mmol), EtOH–CH<sub>2</sub>Cl<sub>2</sub> [2:1] (100 mL), and 40% aq. glyoxal (1.4 mL, 12 mmol). The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent evaporated. Compound 2 (1*R*,2*R*) is a yellow solid, it crystallized from EtOH–CH<sub>2</sub>Cl<sub>2</sub> (8.3 g, 96%). Mp 120–122 °C. [ $\alpha$ ]<sub>D</sub> – 138 (CH<sub>2</sub>Cl<sub>2</sub>, 25 °C). NMR (CDCl<sub>3</sub>, 25 °C  $\delta$  ppm), <sup>1</sup>H: 8.06 (s, 2H, H2), 3.78 (dq, <sup>3</sup>*J* 7.68 and 6.59 Hz, 2H, H3), 4.92 (d, <sup>3</sup>*J* 7.68 Hz, 2H, H4), 1.05 (d, <sup>3</sup>*J* 6.59 Hz, 6H, H5), 7.36 (m, 10H, H–Ph). <sup>13</sup>C: 162.3 (C2), 72.3 (C3), 67.3 (C4), 20.2 (C5), 138.9 (C<sub>i</sub>), 128.7 (C<sub>o</sub>), 128.7 (C<sub>m</sub>), 127.9 (C<sub>p</sub>). IR (KBr,  $\nu_{max}$  cm<sup>-1</sup>): 1632 (C—N), 736 (C–Cl). Anal. calcd for [C<sub>20</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>2</sub>]: C, 66.49; H, 6.14; N, 7.75%; found: C, 66.11; H, 6.18; N, 7.68%.

2,2-Dichloro-1,3-bis[(*S*) 1-methylbenzyl]-1,3-diaza-2-aluminacyclopenta-3,5-diene tetrachloro aluminate (5). A general procedure was used for synthesizing aluminum compounds 5–10. To a solution of compound 1 (0.27 g, 1.0 mmol) in toluene (10 mL) and in a N<sub>2</sub> atmosphere previously cooled at -78 °C, AlCl<sub>3</sub> (0.27 g, 2.0 mmol) dissolved in toluene (10 mL) at -78 °C was added. The resulting mixture was stirred for 2 h. Then, the solution was evaporated and

compound **13** was obtained as a brown solid. Mp. 144–145 °C. IR (KBr,  $\nu_{\rm max}$  cm<sup>-1</sup>) 1647. NMR (THF-d<sub>8</sub>, 25 °C  $\delta$  ppm) <sup>1</sup>H: 8.43 (br s, 1H, H2), 7.40–7.50 (br, 10H, Ph), 6.06 (q, <sup>3</sup>*J* 6.6 Hz, 2H, H3), 1.55 (d, <sup>3</sup>*J* 6.6 Hz, 6H, H4). <sup>13</sup>C: 159.6 (C2), 130–127 (Ph), 62.0 (C3), 21.8 (C4). <sup>27</sup>Al: +107.1 ( $\Delta_{1/2}$  94 Hz), +34 ( $\Delta_{1/2}$  1250 Hz). Anal. calcd for [C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>Al<sub>2</sub>Cl<sub>6</sub>]: C, 40.71; H, 3.80; N, 5.28%; found: C, 40.29; H, 4.34; N, 4.99%.

2,2-Dichloro-1,3-bis[(*R*)-1'-chlorobutan-2'-yl]-1,3-diaza-2-aluminacyclopenta-3,5-diene tetrachloro aluminate (6). Compound 2 (0.27 g. 1.1 mmol) in toluene (10 mL) was added to AlCl<sub>3</sub> (0.30 g, 2.3 mmol) in toluene (10 mL). A brown oil was separated from the reaction mixture and isolated using a canula. Brown solid, mp 119–121 °C. IR (KBr,  $\nu_{max}$  cm<sup>-1</sup>) 1636. <sup>27</sup>Al NMR (THF-d<sub>8</sub>, 25 °C  $\delta$  ppm): +100.1 ( $\Delta_{1/2}$  92 Hz), +62 ( $\Delta_{1/2}$  3036 Hz). Anal. calcd for [C<sub>10</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>2</sub>Al<sub>2</sub>Cl<sub>6</sub>]: C, 23.84; H, 3.60; N, 5.56%; found: C, 23.31; H, 3.68; N, 5.07%.

2,2-Dichloro-1,3-bis[(*S*,*S*)-1'-chloro-1'-phenylpropan-2'-yl]-1,3diaza-2-alumina-cyclopenta-3,5-diene tetrachloroaluminate (7). Compound 3 (0.39 g, 1.1 mmol) in toluene (10 mL) was added to AlCl<sub>3</sub> (0.29 g. 2.2 mmol) in toluene (10 mL). A viscous brown solid was obtained. IR (KBr,  $\nu_{max}$  cm<sup>-1</sup>) 1634. <sup>27</sup>Al NMR (THF-d<sub>8</sub>, 25 °C;  $\delta$  ppm): +100.2 ( $\Delta_{1/2}$  80 Hz), +68 ( $\Delta_{1/2}$  3754 Hz).

2,2-Dichloro-1,3-di-*tert*-butyl-1,3-diaza-2-aluminacyclopenta-3,5-diene tetrachloro aluminate (8). Compound 4 (0.5 g, 3.0 mmol) in toluene (20 mL) was added to  $AlCl_3$  (0.8 g, 6.0 mmol) in toluene (20 mL). Compound 13 is obtained as a yellow solid (0.81 g, 90%). Mp 43 °C. NMR (CDCl<sub>3</sub>, 25 °C;  $\delta$  ppm), <sup>1</sup>H: 9.04 (s, 2H, H2), 1.71 (s, 18H, H4). <sup>13</sup>C: 163.3 (C2), 65.9 (C3), 29.7 (C4). <sup>27</sup>Al: +102.3 ( $\Delta_{1/2}$  150 Hz, Al<sup>-</sup>), +94.6 ( $\Delta_{1/2}$  3550 Hz, Al<sup>+</sup>). (+)TOF, m/z (amu): calcd for [C<sub>10</sub>H<sub>20</sub>N<sub>2</sub>AlCl<sub>2</sub>]: 265.0818; found; 265.0816. (-)TOF, m/z (amu): calcd for [AlCl<sub>4</sub>]<sup>-</sup> 126.9045; found: 126.9055. IR (KBr,  $\nu_{max}$  cm<sup>-1</sup>): 1644 (C=N), 1482 (C-N), 1381 (C-C). Anal. calcd for [C<sub>10</sub>H<sub>20</sub>N<sub>2</sub>Al<sub>2</sub>Cl<sub>6</sub>]: C, 27.61; H, 4.63; N, 6.44%; found: C, 27.11; H, 4.43; N, 6.25%.

**2,2-Diiodo-1,3-di-***tert***-butyl-1,3-diaza-2-aluminacyclopenta-3,5diene tetraiodo aluminate (9).** Compound 4 (0.5 g, 3.0 mmol) in toluene (20 mL) was added to AlI<sub>3</sub> (2.43 g, 6.0 mmol) in toluene (20 mL). Compound **9** is obtained as a brown solid (2.52 g, 85%). Mp 43 °C. NMR (CDCl<sub>3</sub>, 25 °C;  $\delta$  ppm), <sup>1</sup>H: 9.27 (s, 2H, H2), 1.83 (s, 18H, H4). <sup>13</sup>C: 160.0 (C2), 65.2 (C3), 30.6 (C4). <sup>27</sup>Al: +89.4 ( $\Delta_{1/2}$  2050 Hz, Al<sup>+</sup>), -20.2 ( $\Delta_{1/2}$  137.3 Hz, Al<sup>-</sup>). IR (KBr,  $\nu_{max}$  cm<sup>-1</sup>): 1644 (C=N): Anal. calcd for [C<sub>10</sub>H<sub>20</sub>N<sub>2</sub>Al<sub>2</sub>I<sub>6</sub>]: C, 12.21; H, 2.05; N, 2.85%; found: C, 11.88%, H, 2.42; N, 2.96%.

2,2-Dichloro-1,3-di-*tert*-butyl-1,3-diaza-2-aluminacyclopenta-3,5-diene trichloromethyl aluminate (10). Compound 4 (0.5 g, 3.0 mmol) in toluene (50 mL) was added to a 1 M solution of AlMeCl<sub>2</sub> in hexane (6 mL, 6.0 mmol). Compound **15** is obtained as a crystalline solid. Suitable crystals for X-ray diffraction analysis were obtained CHCl<sub>3</sub> (1.03 g, 80%). Dec 50 °C. NMR (CDCl<sub>3</sub>, 25 °C;  $\delta$  ppm), <sup>1</sup>H: 8.98 (s, 2H, H2), 1.62 (s, 18H, H4), -0.53 (s, 3H, AlMe<sub>2</sub><sup>+</sup>), -0.17 (s, 3H, AlMe<sub>4</sub><sup>-</sup>); <sup>13</sup>C: 162.8 (C2), 64.2 (C3), 29.6 (C4), -8.9 (AlMe<sub>2</sub><sup>+</sup>), -8.3 (AlMe<sub>4</sub><sup>-</sup>). <sup>27</sup>Al: +130.1 ( $\Delta_{1/2}$  2016 Hz, Al<sup>+</sup>), +102.1 ( $\Delta_{1/2}$  22.3 Hz, Al<sup>-</sup>). IR (KBr,  $\nu_{max}$  cm<sup>-1</sup>) 1650 (C=N).

1,3-Bis[(S)-methylbenzyl]-2-[N-(S)-methylbenzyl]-methanimineimidazolium tetrachloro aluminate (11). General procedure for imidazoles 11-14. To a solution of diazabutadiene 1 (1.0 g, 3.78 mmol) in THF (50 mL) and in a N2 atmosphere, AlCl3 (0.54 g, 3.78 mmol) in THF (20 mL) previously cooled at -78 °C was slowly added. The reaction mixture was stirred for 2 h at rt; the solvent was evaporated in vacuum. The product was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed with water (5 mL). The organic solution was dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated (1.0 g, 98%). Crystals of 11, suitable for X-ray diffraction were obtained from CHCl<sub>3</sub>. Mp 126–128 °C. NMR (CDCl<sub>3</sub>, 25 °C;  $\delta$  ppm), <sup>1</sup>H: 7.53 (s, 2H, H2), 7.34–6.78 (m, 15H, Ph), 6.17 (q, <sup>3</sup>/ 6.3 Hz, 2H, H3), 1.85 (d, <sup>3</sup>/ 6.3 Hz, 6H, H4), [substituent in C1: 8.43 (s, 1H, H2'), 4.60 (q, <sup>3</sup>J 6.3 Hz, 1H, H3')]. <sup>13</sup>C: 141.9 (C<sub>i</sub>), 137.1 (C1), 129.5 (4C<sub>o</sub>), 129.1  $(2C_p)$ , 126.5  $(4C_m)$ , 121.3 (C2), 59.2 (C3), 21.4 (C4)), [substituent in C1: 143.8 (C2'), 138.2 (2C<sub>i'</sub>), 128.9 (2C<sub>o'</sub>), 127.8  $(C_{p'})$ , 126.9 (2 $C_{m'}$ ), 70.8 (C3'), 23.5 (C5')]. <sup>27</sup>Al: 101.3 ( $\Delta_{1/2}$  215 Hz). IR (KBr,  $\nu_{\text{max}}$  cm<sup>-1</sup>): 1638 [C=N]. (+)TOF, *m/z* (amu): calcd for  $[C_{28}H_{30}N_3]^+$ : 408.2434; found: 408.2436. (–)TOF, *m/z* (amu): calcd. for [AlCl<sub>4</sub>]<sup>-</sup> 126.9045; found: 126.9055. Anal. calcd for (C<sub>28</sub>H<sub>38</sub>N<sub>3</sub>AlCl<sub>4</sub>)<sub>5</sub>(CHCl<sub>3</sub>)<sub>3</sub>: C, 52.28; H, 5.92; N, 6.40%; found: C, 52.33; H, 5.65; N, 6.54%.

1,3-Bis[(*R*)-1'-chlorobutan-2''-yl]-2-[*N*-(*R*)-1"-chlorobutan-2"-ylmethanimine]-imidazolium chloride (12). Compound 3 (0.5 g, 2.12 mmol) in THF (50 mL) was added to AlI<sub>3</sub> (0.86 g, 2.12 mmol) in THF (20 mL), at -78 °C. Compound 12 is obtained as a viscous dark liquid (0.4 g, 75%). [ $\alpha$ ]<sup>25°</sup> =  $-172.4^{\circ}$  (CH<sub>2</sub>Cl<sub>2</sub>, 25°). NMR (CDCl<sub>3</sub>, 25 °C; δ ppm), <sup>1</sup>H: 7.71 (s, 2H, H2), 5.27 (br s, 2H, H3), 3.86 (br s, 4H, H4), 1.99 (br s, 4H, H5), 0.84 (br s, 6H, H6), [substituent in C1: 8.53 (s, 1H, H2'), 4.27 (br s, 1H, H3'), 3.76 (br s, 2H, H4'), 1.94 (br s, 2H, H5'), 0.78 (br s, 3H, H6')]. <sup>13</sup>C 138.7 (C1), 121.2 (C2), 62.0 (C3), 46.2 (C4), 25.4 (C5), 10.0 (C6), [substituent in C1: 145.4 (C2'), 74.0 (C3'), 47.1 (C4'), 26.3 (C5'), 10.2 (C6')]. (+)TOF, *m/z* (amu): calcd for  $[C_{16}H_{27}N_3Cl_3]^+$  366.1265; found: 366.1275.

1,3-Bis[(S,S)-1'-chloro-1'-phenylpropan-2'-yl]-2-[N-(S,S)-1"-chloro-1"-phenylpropan-2"-yl-methanimine]-imidazolium chloride (13). Compound 3 (0.5 g, 1.39 mmol) in THF (50 mL) was added to AlI<sub>3</sub> (0.56 g, 1.39 mmol) in THF (20 mL). Compound 13 is obtained as a dark solid (0.56 g, 88%). Mp 92 °C. [a]<sub>D</sub> +58.82 (CH<sub>2</sub>Cl<sub>2</sub>, 25 °C). NMR (CDCl<sub>3</sub>, 25 °C; δ ppm), <sup>1</sup>H: 8.99 (s, 2H, H2), 7.47–7.27 (m, 15H, Ph), 5.99 (t, J 5.9 Hz, 2H, H3), 5.91 (d, J 7.8 Hz, 2H, H4), 1.55 (d, J 5.9 Hz, 6H, H5), [substituent in C1: 9.11 (s, 1H, H2'), 4.87 (t, J 5.9 Hz, 1H, H3'), 4.08 (d, J 8.5 Hz, 1H, H4'), 0.96 (d, J 5.9 Hz, 3H, H5'). <sup>13</sup>C: 138.5 (C1), 121.9 (C2), 136.5 (2Ci), 129.1 (4Co), 129.0 (2Cp), 127.9 (4C<sub>m</sub>), 65.5 (C3), 61.2 (C4), 18.9 (C5), [substituent in C1: 145.3 (C2'), 138.1 ( $C_{i'}$ ), 129.6 ( $2C_{o'}$ ), 129.0 ( $C_{p'}$ ), 128.1 ( $2C_{m'}$ ), 72.6 (C3'), 67.3 (C4'), 20.3 (C5')]. IR (KBr,  $\nu_{\text{max}}$  cm<sup>-1</sup>): 1737 [C=N], 1677 [C=N], 1554 [C–N]. (+)TOF, m/z (amu): calcd for  $[C_{31}H_{33}N_3Cl_3]^+$ , 552.1734; found, 552.1742. Anal. calcd for (C31H33N3Cl4·3H2O): C, 57.86; H, 6.11; N, 6.53%; found: C, 58.54; H, 6.12; N, 6.65%.

*N-tert*-Butyl-1-[1,3-di-*tert*-butyl-methanimine]-imidazol-1-ium-2-yl triiodide (14). Compound 4 (0.5 g, 3 mmol) in THF (50 mL) was added to  $AII_3$  (1.22 g, 3 mmol) in THF (20 mL). A viscous dark liquid was obtained (0.7 g, 73%).

Crystallization from methanol affords compound **14** with  $I_3$  as the anion. Mp 146–148 °C. (+)TOF, calcd for  $[C_{16}H_{30}N_3]^+$ , *m/z* (amu): 264.2434; found: 264.2435. (–)TOF, calcd. for  $[I]^-$ , *m/z* (amu): 126.9045; found: 126.9048. NMR (CDCl<sub>3</sub>, 25 °C;  $\delta$  ppm), <sup>1</sup>H: 7.43 (s, 2H, H2), 1.59 (s, 18H, H4), [substituent in C1: 8.37 (s, 1H, H2'), 1.31 (s, 9H, H4')] <sup>13</sup>C: 119.5 (C2), 140.2 (C1), 63.1 (C3), 30.2 (C4), [substituent in C1: 145.4 (C2'), 61.4 (C3'), 27.8 (C4')]. IR (KBr,  $\nu_{max}$  cm<sup>-1</sup>): 1641 [C—N], 1596 [C–N]. Anal. calcd for [C<sub>16</sub>H<sub>30</sub>N<sub>3</sub>I<sub>3</sub>·1/2I]: C, 27.12; H, 4.27; N, 5.93%; found: C, 27.42; H, 4.34; N, 6.33%. Crystals were subjected to X-ray diffraction analyses.

Crystallization from CHCl<sub>3</sub> gave compound **14** having AlCl<sub>4</sub> as the anion. (+)TOF, m/z (amu): calcd for [C<sub>16</sub>H<sub>30</sub>N<sub>3</sub>]: 264.2435; found: 264.2437. (–)TOF, m/z (amu): calcd for [AlCl<sub>4</sub>]<sup>-</sup> 126.9045; found: 126.9055. Crystals were subjected to X-ray diffraction analyses.

2,2,2-Trichloro-1,3-di[(*S*) methylbenzyl]-1,3-diaza-2-indacyclopenta-3,5-diene (15). A general procedure was used for compounds 15–18. Compound 15 was prepared at -75 °C in a N<sub>2</sub> atmosphere by addition of a solution of InCl<sub>3</sub> (0.17 g, 0.76 mmol) in dry acetonitrile (10 mL) to a solution of 2 (0.1 g, 0.38 mmol) in dry acetonitrile (10 mL). The solvent was evaporated in vacuum. A brown solid was obtained (0.6 g, 91%). Mp 84–86 °C. NMR (CD<sub>3</sub>CN, 25 °C;  $\delta$  ppm), <sup>1</sup>H: 8.21 (s, 2H, H2), 7.40–7.50 (m, 10H, Ph), 5.75 (q, <sup>3</sup>J 7.0 Hz, 2H, H3), 1.74 (d, <sup>3</sup>J 7.0 Hz, 6H, H4). <sup>13</sup>C: 156.6 (C2), 138.4 (C<sub>i</sub>), 129.1 (C<sub>o</sub>), 128.9 (C<sub>p</sub>), 128.5 (C<sub>m</sub>), 63.0 (C3), 20.6 (C4). IR (KBr,  $\nu$  cm<sup>-1</sup>): 1660, 1628 (C=N, Ph).

2,2,2-Trichloro-1,3-bis[(R) 1'-chlorobutan-2'-yl]-1,3-diaza-2-indacyclopenta-3,5-diene (16). InCl<sub>3</sub> (0.1 g, 0.42 mmol) in

acetonitrile (0.5 mL) was added to compound 2 (0.5 g, 0.21 mmol) in acetonitrile (0.5 mL). A colorless solid (0.1 g, 97%) was obtained. Mp 131–132 °C. NMR (CD<sub>3</sub>CN, 25 °C;  $\delta$  ppm), <sup>1</sup>H: 8.31 (s, 2H, H2), 4.49 (m, 2H, H3), 4.20 (dd, <sup>2</sup>J 12.0, 6.3 Hz, 2H, H4A), 4.09 (dd, <sup>2</sup>J 12.0, 2.9 Hz, 2H, H4B), 2.06 (m, 2H, H5A), 1.93 (m, 2H, H5B), 0.92 (t, 6.0 Hz, 3H, H6). <sup>13</sup>C: 156.2 (C2), 69.2 (C3), 45.9 (C4), 23.7 (C5), 9.8 (C6). IR (KBr,  $\nu$  cm<sup>-1</sup>): 1677, 1617 (C=N). Anal. calcd for [C<sub>10</sub>H<sub>18</sub>N<sub>2</sub>Cl<sub>5</sub>In·1/2CH<sub>3</sub>CN]: C, 29.15; H, 4.48; N, 5.67%; found: C, 29.43; H, 4.56; N, 5.41%.

**2,2,2-Trichloro-1,3-bis**[(*S*,*S*) 1'-chloro-1'-phenylpropan-2'-yl]-**1,3-diaza-2-indacyclopenta-3,5-diene** (17). InCl<sub>3</sub> (0.3 g, 1.4 mmol) in acetonitrile (10 mL), compound 3 (0.5 g, 1.4 mmol) in acetonitrile (10 mL). Crystalline solid (0.73 g, 91%). Mp 122–124 °C. NMR (CD<sub>3</sub>CN, 25 °C,  $\delta$  ppm), <sup>1</sup>H: 8.33 (s, 2H, H2), 7.40–7.37 (m, 10, Ph), 5.08 (d, 2H, H3), 4.12 (m, 2H, H4), 1.27 (d, 6H, H5). <sup>13</sup>C: 158.2 (C2), 139.5 (C<sub>i</sub>), 128.5 (C<sub>o</sub>, C<sub>p</sub>), 128.2 (C<sub>m</sub>), 72.0 (C3), 66.6 (C4), 19.4 (C5). IR (KBr,  $\nu$  cm<sup>-1</sup>): 1633, 1607 (C=N, Ph). Anal. calcd for [C<sub>20</sub>H<sub>22</sub>Cl<sub>5</sub>N<sub>2</sub>In·<sub>1/2</sub>(C<sub>4</sub>H<sub>8</sub>O)]: C, 42.17%, H, 4.18; N, 4.47%; found: C, 41.97; H, 4.65; N, 4.50%.

**2,2,2-Trichloro-1,3-di***-tert*-**butyl-1,3-diaza-2-indacyclopenta-3,5-diene (18).** InCl<sub>3</sub> (1.04 g, 6.0 mmol) in acetonitrile (10 mL) was added to compound 4 (0.5 g, 3.0 mmol) in acetonitrile (10 mL). A pink solid (1.1 g, 96%) was obtained. Mp 113–115 °C. NMR (CD<sub>3</sub>CN, 25 °C,  $\delta$  ppm), <sup>1</sup>H: 8.35 (s, 2H, H2), 1.57 (s, 18H, H4). <sup>13</sup>C: 155.4 (C2), 66.4 (C3), 29.4 (C4). IR (KBr,  $\nu$  cm<sup>-1</sup>): 1675, 1612 (C=N). Anal. calcd for [C<sub>10</sub>H<sub>20</sub>N<sub>2</sub>Cl<sub>3</sub>In]: C, 30.85; H, 5.14; N, 7.20%; found: C, 30.73; H, 5.66; N, 5.63%.

1,3-Di[(S)-methylbenzyl]-imidazolium tetrachloroindate (19). A general procedure was used for compounds 19-22. To a solution of InCl<sub>3</sub> (0.42 g, 1.9 mmol) in THF (20 mL) and in a N<sub>2</sub> atmosphere, compound 1 (0.5 g, 1.9 mmol) in THF (20 mL) was added. The reaction mixture was stirred for 12 h and the solvent evaporated. From the NMR spectra the reaction yield was estimated to be 21%. The solid was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and washed three times with water (10 mL). Compound 19 (20%) was obtained mixed with methylbenzyl ammonium as a brown viscous liquid. NMR (CDCl<sub>3</sub>, 25 °C;  $\delta$  ppm), <sup>1</sup>H: 9.11 (s, 1H, H1), 7.6-7.2 (m, 10H, Ph), 7.14 (s, 2H, H2), 4.55 (q, <sup>3</sup>J 6.8 Hz, 2H, H3), 1.56 (d, <sup>3</sup>*J* 6.8 Hz, 6H, H4). <sup>13</sup>C: 122.4 (C2), 135.0 (C1), 137.2 (C<sub>i</sub>), 129.8 (Co), 129.5 (Cp), 127.2 (Cm), 60.9 (C3), 21.7 (C4). IR (KBr,  $\nu_{\text{max}} \text{ cm}^{-1}$ ): 1647 [C=N], 1611 [Ph]. (+)TOF, m/z (amu): calcd for  $[C_{19}H_{21}N_2]^+$  277.1699; found 277.1703. (–)TOF, m/z (amu): calcd for [InCl<sub>4</sub>]<sup>-</sup> 254.7798, found 254.7754.

**1,3-Bis**[(*R*)-1'-chlorobutan-2'-yl]-imidazolium tetrachloroindate (20). Compound 3 (0.5 g, 2.1 mmol) in THF (20 mL) was added to InCl<sub>3</sub> (0.47 g, 2.1 mmol), in a N<sub>2</sub> atmosphere. The reaction mixture was stirred for 12 h and the solvent evaporated. The solid was dissolved in MeOH. From this solution the 2-chloro-butanamine hydrochloride crystallized and was separated by filtration. Compound **20** is a brown viscous liquid (0.52 g, 98%). NMR (CDCl<sub>3</sub>, 25 °C;  $\delta$  ppm), <sup>1</sup>H: 7.78 (s, 2H, H2), 10.63 (s, 1H, H1), 4.89 (m, 2H, H3), 4.05 (m, 4H, H4), 2.08 (m, 4H, H5), 0.93 (m, 6H, H6). <sup>13</sup>C: 136.9 (C1), 121.8 (C2), 63.8 (C3), 45.5 (C4), 23.5 (C5), 10.2 (C6). IR (KBr,  $\nu_{max}$  cm<sup>-1</sup>): 1628, 1551 and 1460. (+)TOF, *m/z* (amu): calcd for [C<sub>11</sub>H<sub>19</sub>N<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> 249.0919, found 249.0924. (–)TOF, m/z (amu): calcd for  $[InCl_4]^-$  254.7798; found 254.7802. Anal. calcd for  $[C_{11}H_{19}N_2Cl_6In]$ : C, 26.07; H, 3.78; N, 5.53%; found: C, 25.88; H, 4.07; N, 5.86%.

**1,3-Bis**[(*S*,*S*)-1'-chloro-1'-phenylpropan-2'-yl]-imidazolium tetrachloroindate (21). Compound 2 (0.5 g, 1.4 mmol) in THF (20 mL) was added to InCl<sub>3</sub> (0.31 g, 1.4 mmol) in THF (20 mL), in a N<sub>2</sub> atmosphere. The mixture was stirred for 12 h and the solvent was evaporated. The resulting solids were dissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed with water. In the organic solvent, compound 21 was obtained as a brown solid (0.1 g, 25%). Mp 104–106. NMR (CDCl<sub>3</sub>, 25 °C;  $\delta$  ppm), <sup>1</sup>H: 8.92 (s, 1H, H1), 8.08 (s, 2H, H2), 7.7–7.1 (m, 10H, Ph), 4.91 (m, 1H, H3), 4.03 (br s, 1H, H4), 1.07 (br s, 3H, H5). <sup>13</sup>C: 121.2 (C2), 138.4 (C1), 137.9 (C<sub>i</sub>), 130.2 (C<sub>o</sub>), 129.8 (C<sub>p</sub>), 128.5 (C<sub>m</sub>), 64.3 (C4), 53.5 (C3), 15.8 (C5). IR (KBr,  $\nu_{max}$  cm<sup>-1</sup>): 1669, 1633 and 1453. (+)TOF, *m*/*z* (amu): calcd for [C<sub>21</sub>H<sub>23</sub>N<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> 373.1232, found 373.1231. (–)TOF, *m*/*z* (amu): calcd for [InCl<sub>4</sub>]<sup>-</sup> 254.7798; found 254.7794. Anal. calcd for [C<sub>21</sub>H<sub>23</sub>N<sub>2</sub>Cl<sub>3</sub>·H<sub>2</sub>O]: C, 58.96; H, 5.89; N, 6.55%; found: C, 58.73; H, 5.82; N, 6.60%.

**1,3-Bis**[*tert*-butyl]-imidazolium tetrachloroindate (22). Compound 4 (0.5 g, 3 mmol) in THF (20 mL) was added to InCl<sub>3</sub> (0.67 g, 3 mmol) in THF (20 mL), in a N<sub>2</sub> atmosphere. The mixture was stirred for 12 h and the solvent was evaporated. From the NMR spectra the reaction yield was estimated to be 25%. NMR (CDCl<sub>3</sub>, 25 °C;  $\delta$  ppm) <sup>1</sup>H: 7.37 (s, 2H, H2), 8.27 (s, 1H, H1), 1.30 ppm (s, 18H, H3); <sup>13</sup>C: 120.7 (C2), 130.2 (C1), 60.4(C3), 29.6 ppm (C4)]. Mass spectrometry {(+)TOF, *m/z* (amu): calcd for [C<sub>11</sub>H<sub>21</sub>N<sub>2</sub>]<sup>+</sup> 181.1704; found 181.1705. (-)TOF, *m/z* (amu): calcd for [InCl<sub>4</sub>]<sup>-</sup> 254.7798; found 254.7754}.

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