**Supplementary material:**

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

**H. Rojas-Sáenz, G. V. Suárez-Moreno, I. Ramos-García, A. M. Duarte-Hernández, E. Mijangos, A. Peña-Hueso, R. Contreras and A. Flores-Parra***

*Department of Chemistry, Cinvestav, AP 14-740, CP 07000, México DF.*
*e-mail: aflores@cinvestav.mx*

INDEX:

S1 Discussion of the X-ray diffraction analyses of (R) 1-chloro-butan-2-amine hydrochloride.

S2 Macromolecular helix arrangement in the crystal of compound **2**.

S3 Theoretical conformational analysis of 1,4-dialkyl-1,4-diazabutadienes **1**-**4**.

S4 X-Ray diffraction structure of compound **10**.

S5 Cell packing representation of compound **14** with $[I_3]^-$ as anion.

S6 Optimized structures of compounds: **5**, **17**, **18**, **20**-**22**.

S7 Representation of the electrostatic potentials of the indium compounds **16**-**18** and of the ligand **3** coordinated to one and two $InCl_3$ molecules.

## S1: X-Ray diffraction analysis of (R)-2-chloro-butanamine hydrochloride

The (R)-2-chloro-butanamine hydrochloride was crystallized from $CHCl_3$ and the X-ray diffraction structure obtained. The unit cell contains only one ionic pair, Fig 1a. The chloride forms six hydrogen bonds, three with C-H protons (CH···Cl distances 3.05, 2.89 and 2.90 Å); two with the N-H of two molecules, the five hydrogen bonds are almost in the same plane (NH···Cl distances 2.37 and 2.35 Å), Fig. 1b. The ionic pair forms a planar macromolecular arrangement by Cl···H hydrogen bonds, Fig. 2. Planes are connected between them by perpendicular strong N-H···Cl (2.28 Å). Quite interesting is to find that the $CH_2$-Cl chlorine atom does not have any interaction with other protons.

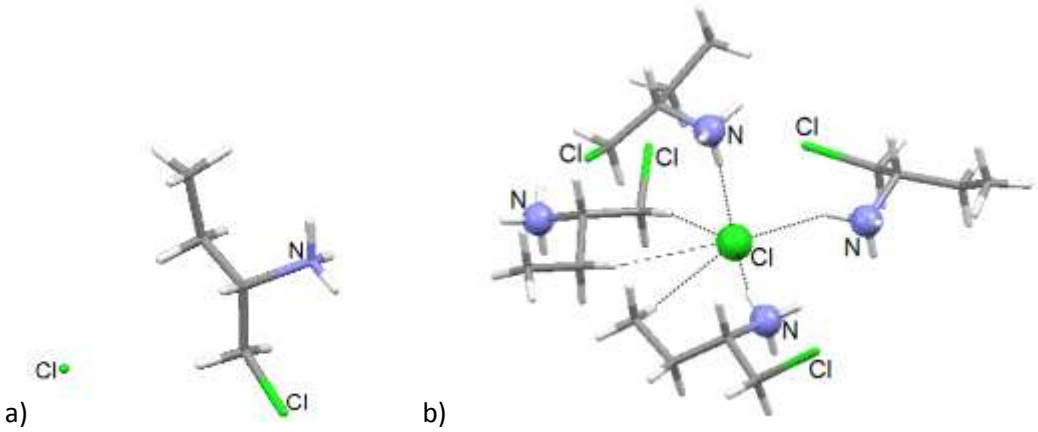
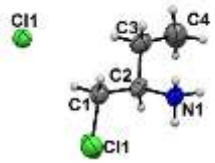
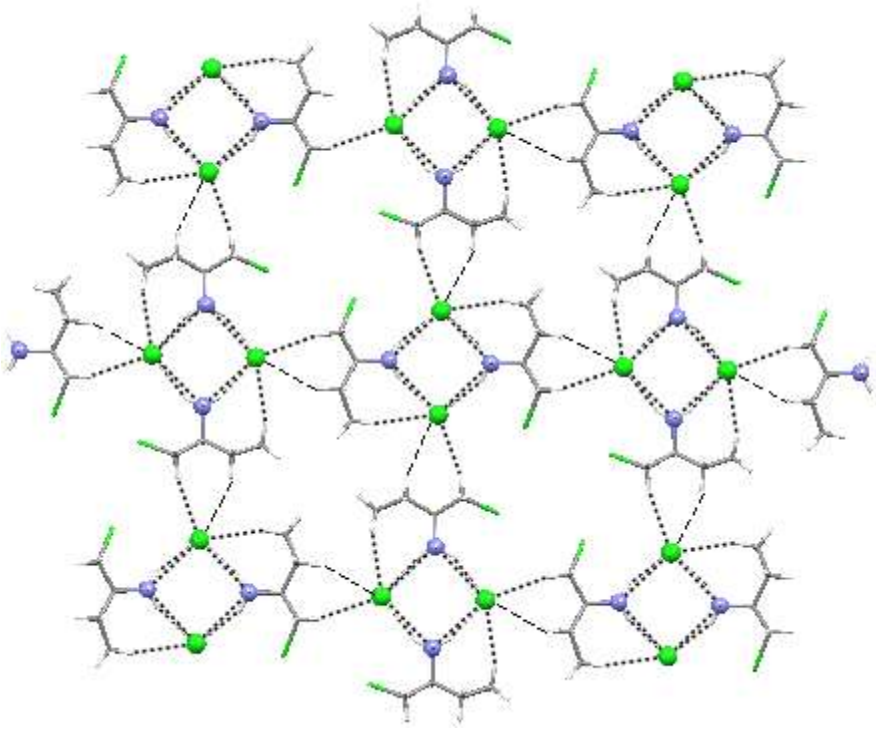



Fig.1. a) Structure of the (S)-2-chloro-butanamine hydrochloride found in the solid state. b) Hydrogen bonds of chloride in the cell of (S)-2-chloro-butanamine hydrochloride

Table of selected bond length and angles of (R) (-)-1-chloro-butan-2-amine hydrochloride

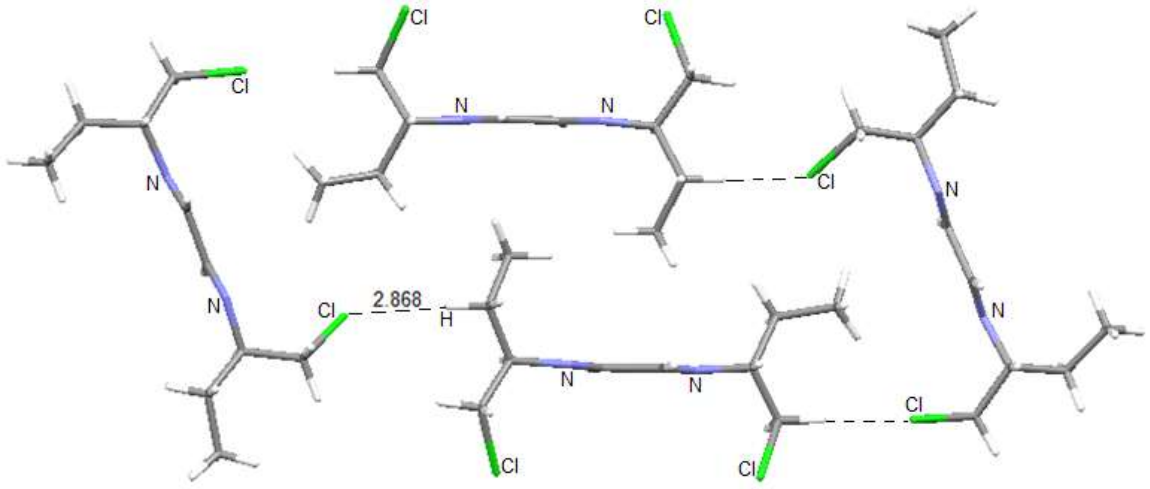



| Bond lengths | | C1-C2 | 1.510(2) |
|---|---|---|---|
| C1-C2 | 1.510(2) | Bond angles | |
| C1-Cl1 | 1.785(2) | C2-C1-Cl1 | 112.4(1) |
| C2-C3 | 1.522(2) | N1-C2-C1 | 109.1(1) |
| C3-C4 | 1.522(3) | N1-C2-C3 | 109.9(1) |
| C2-N1 | 1.496(2) | C1-C2-C3 | 109.9(1) |



The ionic pair of the (S)-2-chloro-butanamine hydrochloride forms a planar macromolecular array by the chloride hydrogen bonds, chloride and nitrogen atoms are represented by spheres.

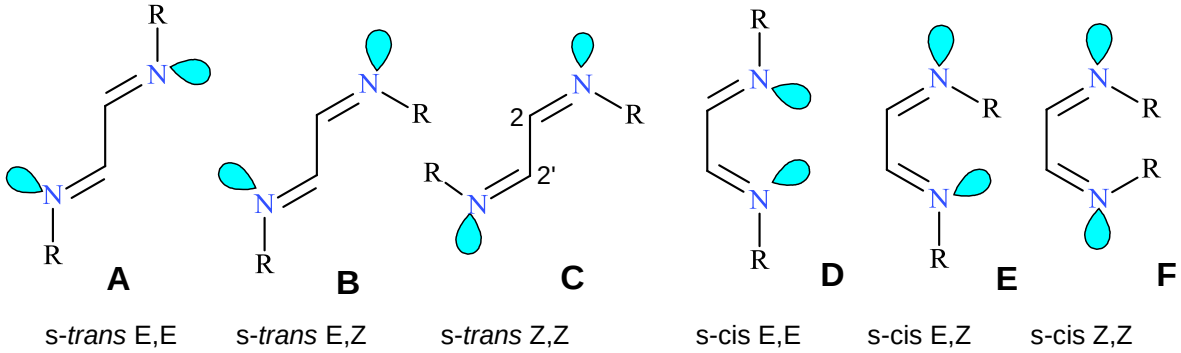
## S2 Macromolecular helix arrangement in the crystal of compound 2:




. Interactions are due to the Cl···H-C hydrogen bonds (2.868 Å). Diazabutadienes are arranged in a helix, with a path of four molecules. The helix axis is perpendicular to the paper plane.

## S3 Theoretical conformational analysis of 1,4-dialkyl-1,4-diazabutadienes 1-4

Six planar conformers (A-F) can be described for compounds **1**-**4**, Scheme 4. Diazabutadienes A, B and C differ by the nitrogen configuration; their interconversion needs only nitrogen inversion. Same situation exits for isomers D-F. Rotation of C2-C2' bond transforms A, B and C into conformers D, E and F, respectively.




Scheme 4. Six planar conformers can be depicted for diazabutadienes **1**-**4**.

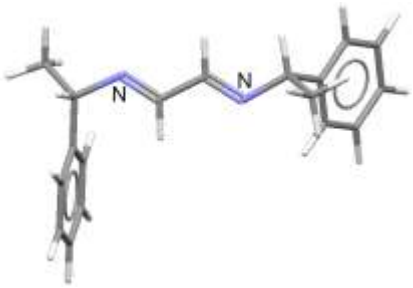
It was relevant to know about the energy difference between conformers. Their free energy is related to the steric effects of the tertiary or quaternary N-substituent. The different conformers were calculated by DFT and the hybrid method B3LYP/6-31+G(d,p). In the four molecules **1**-**4**, isomers A were the most stables. The energy difference (kJ/mol) between A considered as 0.0 and their conformers were calculated, Table. The increase in energy is related to the number of Z relationships: A < B < C. The *cis* conformers (D-F) of compounds **1**-**3** bearing tertiary N-C carbon atoms are 24.4 – 27.1 kJ/mol less stable than A conformers, whereas the *tert*butyl groups in compound **4** makes isomer D less stable than A by 30.4 kJ/mol. The repulsion of the nitrogen lone pairs in isomer D is also a destabilization factor. In all cases, the calculated energy of the C2-C2' rotational bond barrier for **1**-**4** is 37.0 kJ/mol. The steric tension in some of the *cis* conformers did not allow getting the planar conformation, these cases are marked with an asterisk. Calculated molecules are in Figure.

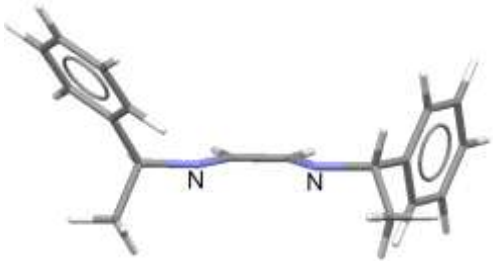
Table Energy difference ($\Delta G^{o}$, kJ/mol) between conformers A and B-F.

| | **A** | **B** | **C** | **D** | **E** | **F** |
|---|---|---|---|---|---|---|
| **1** | 0.0 | 14.9 | 37.9 | 27.1 | 35.8 | -- |
| **2** | 0.0 | 19.0 | 45.6 | 24.4 | 41.2* | 96.2 |
| **3** | 0.0 | 20.3 | 44.4* | 25.6 | 75.5* | 91.5 |
| **4** | 0.0 | 39.2 | 70.3 | 30.4 | 53.4* | 179.1* |

(*) conformers where the steric effect did not allow to get planar diazabutadienes

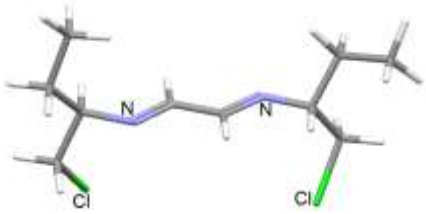
Conformer **A** Conformer **D**

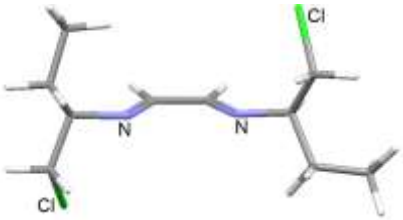



N---N 2.889 Å

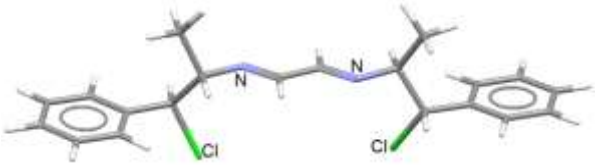
Compound **1**

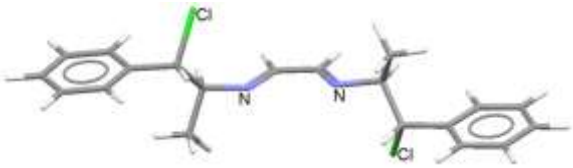



N---N 2.892 Å

Compound **2**




N---N 2.891 Å

Compound **3**

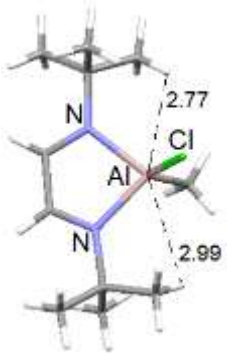


N---N 2.886 Å

Compound **4**

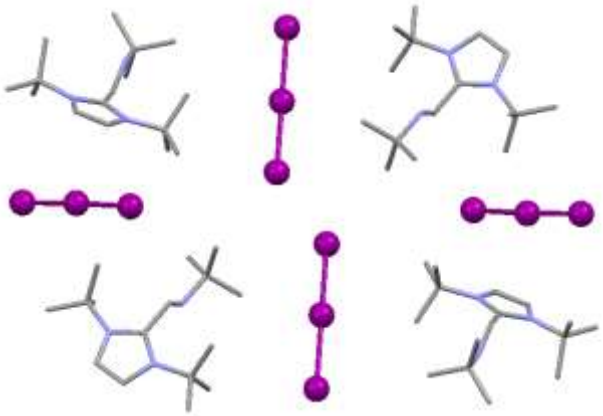
Representation of calculated A and D conformers for compounds **1**-**4**. The N—N distances in cis compounds are shown.

## S4 X-Ray diffraction structure of compound 10



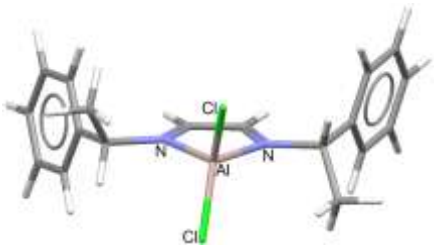

Anagostic interactions H···Al are shown.

## S5 cell packing representation of compound 14 with $[I_3]^-$ as anion

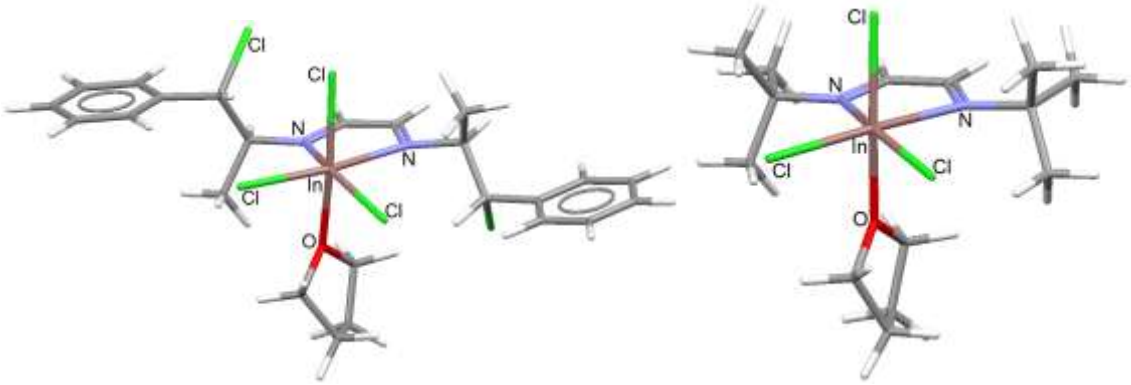


Ball and stick representation of the $[I_3]^-$ anions in the crystal of imidazolium **14**. $[I_3]^-$ Bond lengths: I1-I2, 2.962(2); I2-I3, 2.892(2); and angle: I3-I2-I1, 177.9(1).

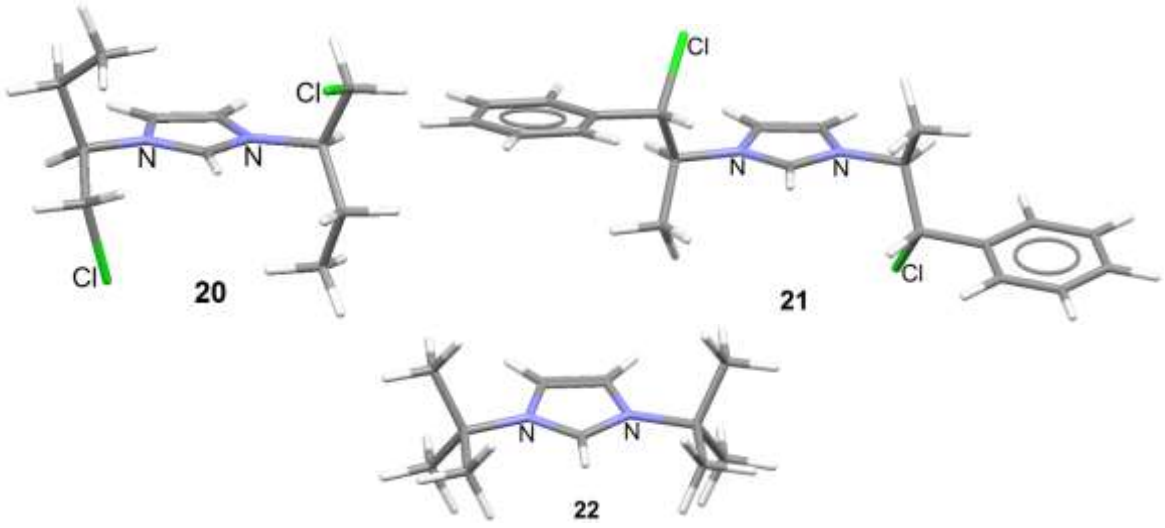
## S6 Optimized structures of compounds 5, 17, 18, 20-22




Calculated structure of compound **5**

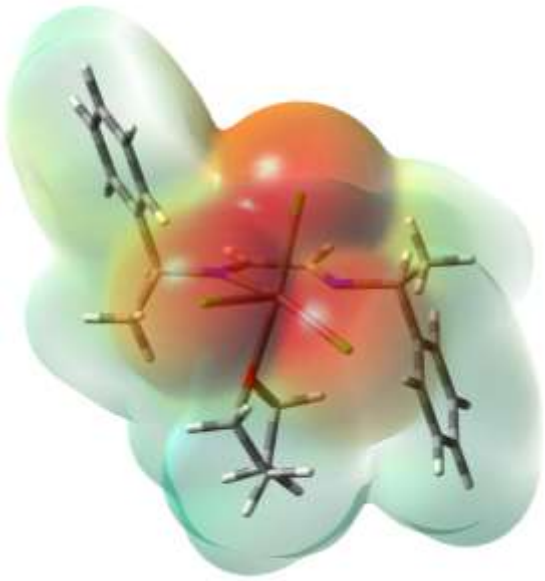



Calculated structures of compounds **17** and **18**.

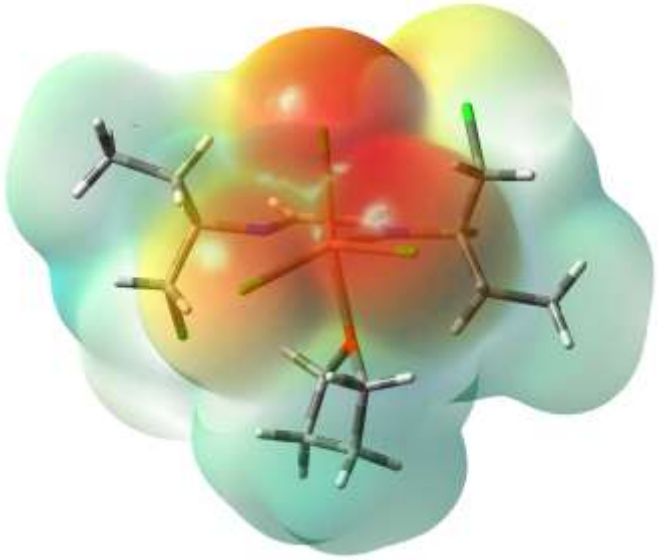



Calculated minimum energy conformers of compounds **20** and **21**.

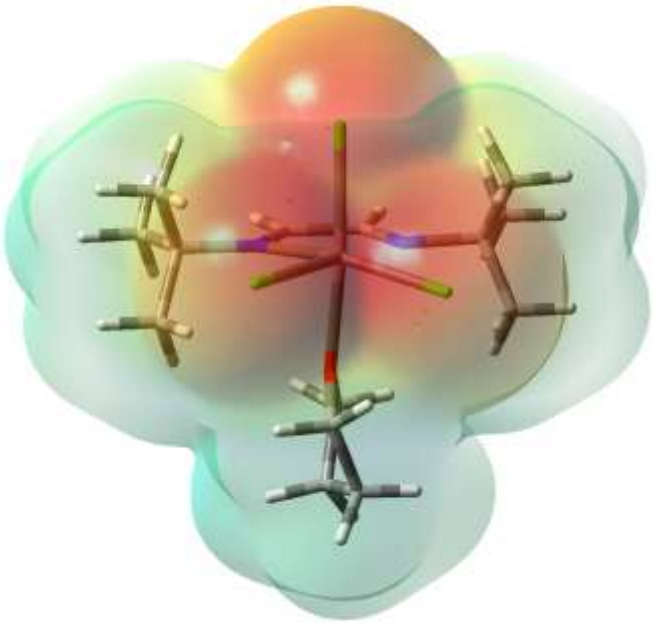
## S7 Calculated electrostatic potential for indium compounds



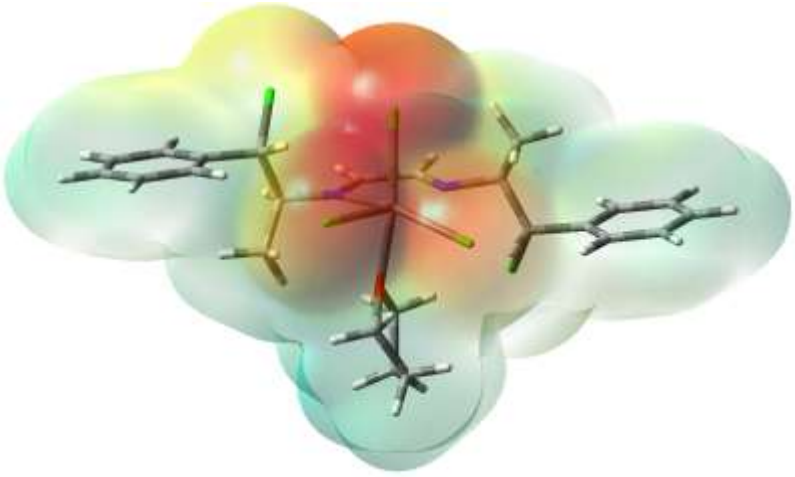
Calculated electrostatic potential for indium compound **15**.



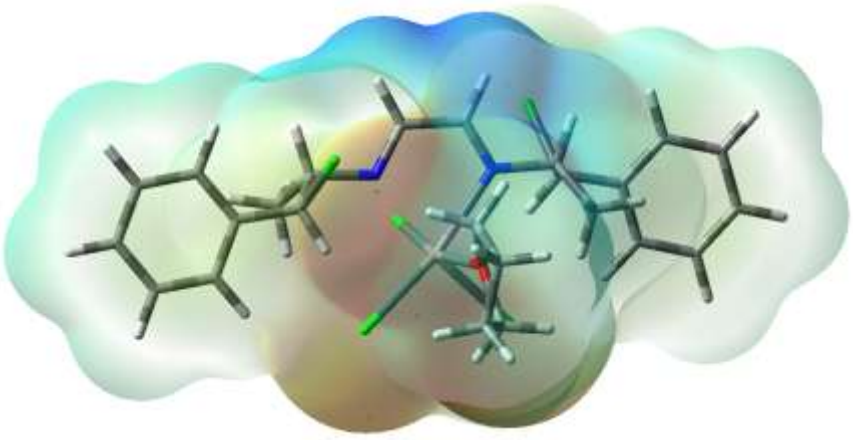
Calculated electrostatic potential for indium compound **16**.



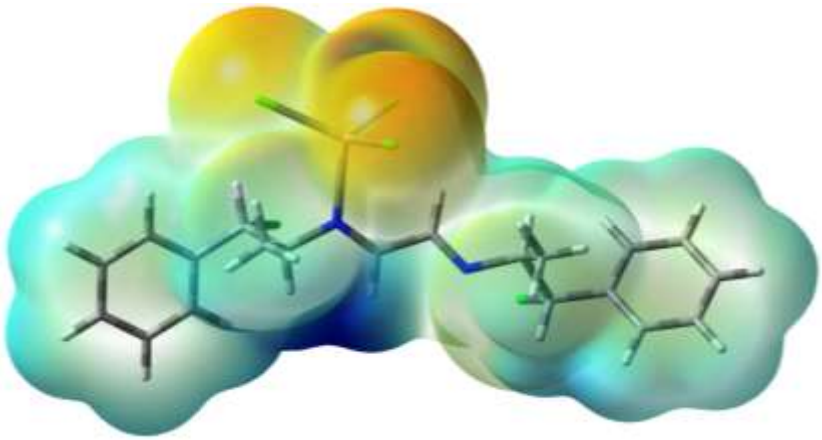
Calculated electrostatic potential for indium compound **18**.



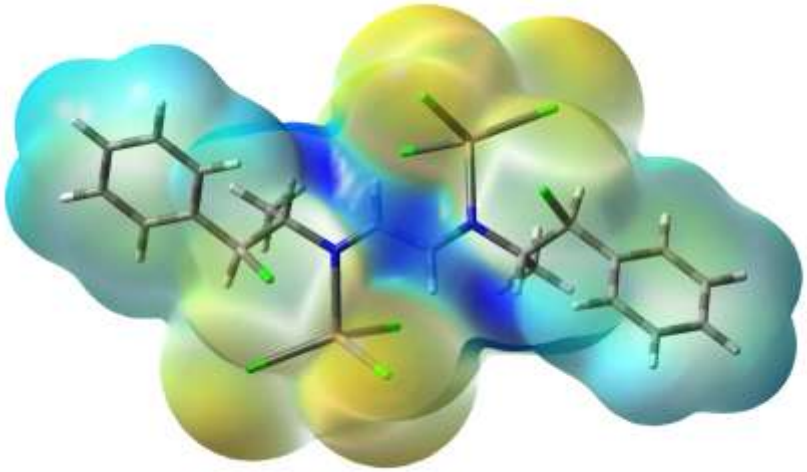
Calculated electrostatic potential for the indium compound **17**.



Calculated electrostatic potential for indium compound **17**. The blue area belongs to the butadiene protons.



Calculated electrostatic potential for ligand **3** coordinated to one $InCl_3$.



Calculated electrostatic potential for ligand **3** coordinated to two $InCl_3$