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Interaction of an imidazolium-2-amidinate (NHC-CDI) zwitterion with zinc dichloride in dichloromethane: role as ligands and C-Cl activation promoters

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1. Experimental Methods.

All manipulations were performed under inert atmosphere using Schlenk-line techniques (O_2 < 3 ppm) and a glove box (O_2 < 0.6 ppm) MBraun MB-20G. Solvents were purified using an MBraun Solvent Purification System. $ZnCl_2$ and PhBr were purchased from Fluorochem and Sigma-Aldrich and used as received. All NMR scale experiments were carried out sample tubes with air-tight PTFE valves. Deuterated solvents were degassed and stored in the glove box in the presence of molecular sieves (4 Å). NMR spectra were recorded with a Bruker 400 Ultrashield (^{1}H 400 MHz, ^{13}C 101 MHz) at room temperature. All chemical shifts were determined using residual signals of solvents and were referenced with regard to external $SiMe_4$. Assignments of spectral signals was helped with 2D (^{1}H-^{1}H COSY, and ^{1}H-^{13}C HSQC and HMQC) NMR experiments. ESI-MS spectra were recorded from dichloromethane solutions using a Bruker Esquire 6000 spectrometer with direct sample injection (IIQ). Elemental analyses were performed with a PerkinElmer 2400 HNS/O analyser Series II (UAH) or LECO TruSpec CHNO (IIQ) and were the average of at least two independent measurements. The NHC-CDI adduct **L** was prepared as reported in the literature.[1]

2. Reaction of the NHC-CDI adduct L with $ZnCl_2$ in CD_2Cl_2.

These reactions were studied *in situ* using ^{1}H NMR spectrometry. Two series of experiments were carried out in which the **L**/$ZnCl_2$ ratio was either 1:1 or 3:2, at different temperatures, from room temperature to 60 ºC. In every case, the ^{1}H NMR spectra of the mixtures showed the same signals shown in Fig. 1 (seen main text), but the relative intensities may change significantly depending upon the precise experimental conditions. Some representative examples are described below.

Example A: A gastight NMR tube was charged with grounded $ZnCl_2$ (4 mg, 0.029 mmol) and **L** (13 mg, 0.029 mmol) dissolved in CD_2Cl_2 was added. Zinc chloride does not dissolve readily, therefore the solution was warmed slightly (placing the tube under a stream of warm) to facilitate the reaction. A ^{1}H NMR spectrum showed that the signals of **1** (Cy-C(1)H signal at δ 3.66 ppm) were prevalent. The sample was allowed to stand at room temperature for 24 h, after which time some crystalline material deposited. Although the crystals diffracted poorly, a low-quality X-ray structure was determined, corresponding to an ionic solid containing $\mathbf{ZnCl_4}$ anions and what seemed a $\mathbf{ZnL_3}$·cation. The crystalline material was insoluble in CD_2Cl_2 and attempts to confirm its identity with **1** were inconclusive.

^{1}H NMR for **1** (400 MHz, CD_2Cl_2, signals selected from the spectrum of the reaction mixture): δ 0.50 - 2.0 ppm, complex multiplets for Cy groups); 2.22 (s, 18 H, *p*-Me); 3.66 (m, 6H, 1-C*H* Cy); 6.58, (d, J_{HH} =8.1 Hz, 12 H, C*H* Tolyl); 6.96 (d, J_{HH} =8.1 Hz,12 H, C*H* Tolyl); 7.53 (s, 6H, C*H* Imidz).

Example B: A solution **L** (7 mg, 0.014 mmol) in 0.7 mL of CD_2Cl_2), that had been lying at the room temperature for a week in the glove box, was mixed with $ZnCl_2$ (2 mg, 1:1 ratio). Large crystals

of **2·Zn_2Cl_6** were noticeable after some time, and they were allowed to grow. After 72 h, these were collected, and used for the X-ray structure determination. A sample of these crystals was dissolved in CD_2Cl_2, and the ^{1}H NMR spectrum confirmed that the Cy-C(1)H signal at δ 3.44 ppm belongs to the spectrum of **2**. ^{1}H NMR Data for **2·Zn_2Cl_6** (400 MHz, CD_2Cl_2, 25 ºC, signals selected from the spectrum of the reaction mixture). δ 0.77 - 1.88 (overlapping multiplets, Cy); δ 1.05 (m, 8H, Cy), 1.23 (m, 8H, Cy), 1.44 (m, 4H, Cy), 1.62 (m, 4H, Cy), 1.70 (m, 6H, Cy), 1.80 (m, 6H, Cy), 2.24 (s, 6H, *p*-Me), 2.37 (s, 6H, *p*-Me), 3.46 (m, 4H, 1-CH Cy), 6.27 (d, 4H, J_{HH} =8.2 Hz, C*H* Tolyl); 7.04 (two overlapping doublets, 8H, C*H* Tolyl); 7.28 (d, 4H, J_{HH} =8.0 Hz, C*H* Tolyl); 7.71 (s, 4H, C*H* Imidz.). ^{13}C RMN {1H} (100MHz, CD_2Cl_2, 25 ºC) δ 20.9 (*p*-Me), 21.2 (*p*-Me), 24.6 (4-CH_2, Cy), 25.7 (3-CH_2, Cy), 25.8 (3´-CH_2, Cy), 33.1 (2-CH_2, Cy), 33.2 (2´-CH_2, Cy), 60.3 (1-CH, Cy), 121.1 (CH, Imidz), 123.8 (*o*-CH, *p*-Tol), 127.0 (*o*-CH, *p*-Tol), 130.8 (*m*-CH, *p*-Tol), 130.9 (*m*-CH, *p*-Tol), 132.7 (C, Imidz), 136.0 (*p*-C, *p*-Tol), 136.1 (*p*-C, *p*-Tol), 139.6 (i*pso*-C, *p*-Tol), 139.9 (*ipso*-C, *p*-Tol), 142.6 ($C(NAr)_2$).

Example C: 2 mg (0.014 mmol) of $ZnCl_2$ and 10 mg (0.022 mmol) of $ICyCDI^{pTol}$ were suspended in CD_2Cl_2 (3:2 ratio). The mixture was shacked, and allowed to rest at room temperature, taking ^{1}H NMR spectra at different times; selected spectra are shown in Figure 1 (A - C) in the main text. A deposit of crystalline material was formed after 4 days.

3. Reaction of L with $ZnCl_2$ in PhBr. Synthesis of [ZnL_3][$ZnCl_4$] (1·$ZnCl_4$).

To a suspension of 0.10 g (0.022 mmol) of **L** in 25 ml of bromobenzene, 0.02 g (0.015 mmol) of $ZnCl_2$ were added. The mixture was heated at 80 ºC for 3 days in a PTFE-valved ampoule. The solution was let to slowly cool down to room temperature. Crystals were formed, that were filtered off. At this point, crystals were sampled and submitted for X-ray diffraction analysis that confirmed the **[ZnL_3][$ZnCl_4$]** composition. The solid was washed with hexane and dried under vacuum. Yield: 0.07 g, 59%. No satisfactory analysis could be obtained, possibly due to the presence of small amounts of unreacted $ZnCl_2$ or fractional amounts of crystallization solvent (PhBr).

4. Preparative syntheses of 2·Cl-d_2 and 2·Cl

2·Cl-d_2. A solution of 20 mg of the betaine (L) in dichloromethane-d_2 was transferred to a gas-tight NMR tube and heated for 24 h at 60 ºC. At the final point, the colour was faint yellow. The ^{1}H spectrum showed full conversion to **2·Cl-d_2**. ^{1}H NMR (400 MHz, CD_2Cl_2, 25ºC): δ 0.87 (m, 4H, Cy); 0.99 - 1.19 (complex m, 12 H, Cy); 1.27 (m, 4H, Cy); 1.61 - 1.78 (complex m, 12 H, Cy); 4.05 (m, 4H, Cy); 2.25 (s, 6 H, *p*-Me); 2.38 (s, 6H, *p*-Me); 3.52 (m, 4H, 1-C*H* Cy); 6.29 (d, J_{HH} = 8.2 Hz, C*H* Tolyl); 7.04 (two overlapping doublets, 8H, C*H* Tolyl); 7.27 (d, J_{HH} = 8.0 Hz, C*H* Tolyl); 8.22 (s, 4H, C*H* Imidz.). ESI-MS: m/z 462.4, $L_2CD_2^{2+}$.

2·Cl: *Method 1:* The above-described procedure was applied for the preparative synthesis of this product with natural isotopic abundances, starting from 20 mg of **L** (0.044 mmol), in 10 mL of CH_2Cl_2, affording the product in essentially quantitative yield. Yield, 17 mg (0.018 mmol), 84 %. *Method 2:* 0.15 g of $ICyCDI^{(p\text{-Tol})}$ were dissolved in 15 mL of CH_2Cl_2 and stirred for 6 days at 30ºC in a PTFE-valved ampoule. The solvent was evaporated to dryness under vacuum, leaving a pale yellow solid that was washed with hexanes and dried under vacuum. Yield, 0.14 g, 85%.

^{1}H NMR (400 MHz, CD_2Cl_2, 25ºC): δ 0.86 (m, 4H, Cy), 0.99 – 1.19 (complex m, 12 H, Cy), 1.29 (m, 4H, Cy), 1.55 (m, 4H, Cy), 1.60 – 1.79 (complex m, 12 H, Cy), 1.85 (m, 4H, Cy), 2.25 (s, 6H, *p*-Me), 2.37 (s, 6H, *p*-Me), 3.49 (m, 4H, 1-CH Cy), , 6.29 (d, 4H, $^3J_{HH}$= 8.3 Hz, *m*-C*H* Tol-1), 6.97 (s, 2H, C*H*$_2$) 7.04 (two overlapping d, 8H, *m*+*o* C*H* Tol-1 and Tol-2, resp.), 7.26 (d, 4H, $^3J_{HH}$= 8.1 Hz, *m*-CH Tol-2), 8.21 (s, 2H, C*H* Imidz); ^{13}C {^{1}H} (100 MHz, CD_2Cl_2, 25 ºC) δ 20.8 (*p*-Me), 21.2 (*p*-Me), 24.6 (4-CH_2, Cy), 25.8 (3-CH_2, Cy), 25.8 (3´-CH_2, Cy), 33.1 (2-CH_2, Cy), 33.3 (2´-CH_2, Cy) 60.4 (1-CH, Cy), 60.9 (CH_2),121.0 (*m*-*C*H Tol-1), 123.5 (*C*H Imidz), 127.1 (*o*-*C*H Tol-2), 130.7 (*m*-*C*H Tol-1), 130.8 (*m*-*C*H Tol-2), 133.1 (*C* Imidz), 136.0 (*C*-N, Tol-2), 136.1 (*C*-N, Tol-1), 139.6 (*C*-Me, Tol-2), 139.7 (*C*-Me Tol-1), 142.7 (*C*N_2). ESI-MS: m/z 461.4, $L_2CH_2^{2+}$. Elemental Analysis Calculated for $C_{61}H_{78}N_8Cl_2$: C, 73.69; H, 7.91; N, 11.27. Found: C, 73.50; H, 7.97; N, 11.32.

5. Comparison of the reaction rate of L with CD_2Cl_2 with and without added $ZnCl_2$.

A solution containing 20 mg (0.044 mmol) in 0.14 mL of CD_2Cl_2 was split in two halves, and each one was transferred into an NMR tube, one of which was loaded with 2 mg of $ZnCl_2$ (0.014 mmol) and the other was not. This operation resulted in two identical samples one of them containing a mixture of the betaine and $ZnCl_2$. After recording the ^{1}H NMR spectra of both samples, these were placed in a thermostatic bath at 40 ºC, from which they removed periodically over two days to repeat the measurements (these operations were done simultaneously for both samples). The progress of the reactions was monitored measuring the intensity of the Cy-C(1)H signals of both the starting betaine and the products. The $ZnCl_2$-containing sample was turbid over the entire experiment, as $ZnCl_2$ did not fully dissolve from the beginning, and a crystalline solid precipitated in the later stages. In contrast, the $ZnCl_2$-free sample remained clear throughout the entire experiment. Figure S1 shows, on the left side, the percent of betaine consumed over the time in each experiment. As can be seen, the consumption of the starting material is only slightly faster in the presence of $ZnCl_2$ (orange) than without it (blue), which can be attributed to the sequestration of some ligandin **1**. The plot on the left side shows the buildup of products. It can be seen that the buildup of **2** is slightly slower in the presence of $ZnCl_2$, and nearly stops when **L** becomes sequestrated in the sparingly soluble zinc complex. After 20 h, the amount of free betaine increases very slightly, but the concentration of the Zn complex decreases, as it precipitates out from the solution. The sum of both

products (solid orange line) falls below the line corresponding to the experiment in the absence of $ZnCl_2$ (solid blue line), notwithstanding the similar advance of both reactions in terms of product consumption.

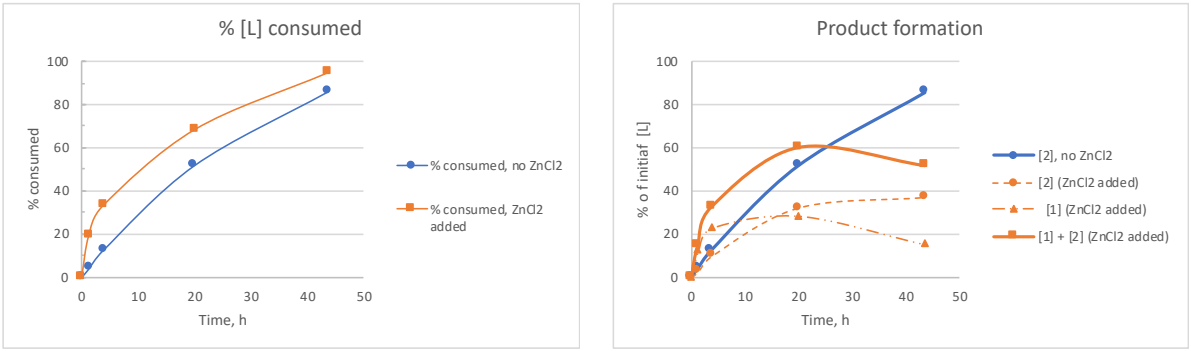


Figure S1. Effect of $ZnCl_2$ on reaction of **L** with CD_2Cl_2 at 40 ºC. Left side, percent of betaine consumed over the time: orange, in the presence of $ZnCl_2$ (**L**:Zn = 3:2); blue, in the absence of $ZnCl_2$. Right, product formation: orange lines, in the presence of $ZnCl_2$, dashed lines for individual products, solid for the sum [1]+ [2]. Solid blue line, dichloromethane activation in the absence of $ZnCl_2$.

Figure S2 shows a logarithm plot of the relative conversion of the betaine in the absence of $ZnCl_2$. Assuming that, in the absence of $ZnCl_2$, the transformation of betaine **L** into $[\mathbf{2}]^{2+}$ in CD_2Cl_2 as the solvent is a double nucleophilic substitution process, with the rate being controlled in the first step, it can be readily shown that the overall kinetics should obey pseudo-first order kinetics, independently of the kinetic nature of the second step. Assuming that the first step corresponds to a S_N2-type reaction, the apparent, pseudo-first order constant (k_{app}) incorporates the solvent (dichloromethane) concentration and twice the real second-order constant of the rate-limiting step (because two mole of the starting betaine are incorporated in the final product), as shown in Ecs S1 and S2.

$$rate = k_{app}[\mathrm{L}] \qquad (1)$$

$$k_{app} = 2k_1[CD_2Cl_2] \qquad (2)$$

Therefore, it was expected that a plot of $Ln([L]_{t=0}/[L]_t)$ *vs.* time (t) should be linear. However, as can be seen in Figure 2, the experimental data points deviate from first-order kinetics, the betaine being consumed faster than expected. Most likely, this is a bulk effect of the polariry of the reaction medium. The second order rate constant increases as the ionic product $[L_2CD_2]^{2+}\cdot 2[Cl]^-$ accumulates, increasing the ion strength, hence the medium polarity. The rate constant (k_{app}) in dichloromethane would correspond to the initial rate constant (t =0). This was obtained by fitting the data series to a 2nd order polynomial dependency on time (namely, $a\cdot t^2+b\cdot t+c$). The initial slope of the curve (dotted straight line), that gives the value of k_{app}, corresponds to the linear coefficient of the linear term ("*b*") of the polynomial *i. e*, 8.15 x 10^{-6} $s^{-1.}$ (since the first derivative, $2a\cdot t + b$, equals *b* for *t* = 0).

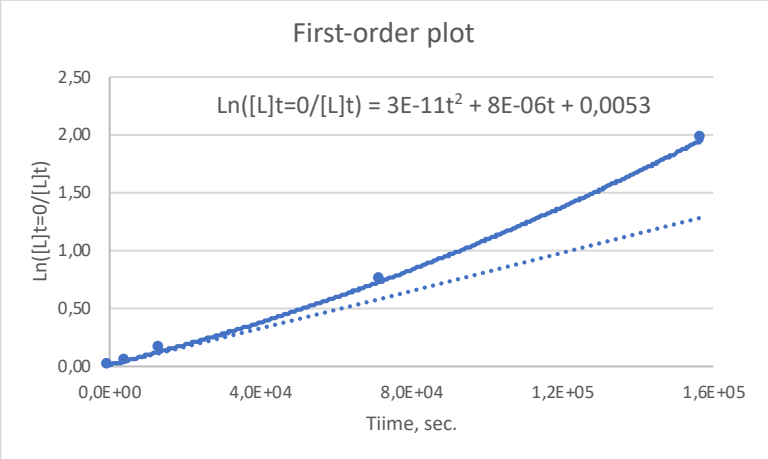


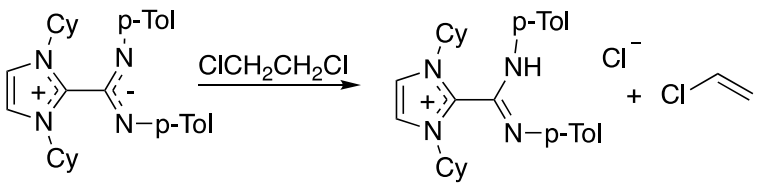
Figure S2. First order (logarithm) plot of betaine consumption in the absence of $ZnCl_2$. The points have been fitted to a quadratic polynomial (shown in the inset), with the first-order coefficient providing the initial slope of the curve (dotted line).

Using Eq (2) and taking the molar concentration of dichloromethane-d_2 as 15.84 M, the initial value for the second order rate constant is $k_1 = k_{app}/2[CD_2Cl_2] = 2.57\text{x}10^{-7}$ $L{\cdot}Mol^{-1}s^{-1}$. To calculate the experimental energy barrier $\Delta G^{\ddagger}$ cited in the main text (27.8 $Kcal{\cdot}mol^{-1}$) , the k_1 value and the reaction temperature (313 K) were fed into the well-known Eyring relationship (3).

$$k_1 = \frac{k'T}{h} e^{-\Delta G^{\ddagger}/RT} \qquad (3)$$

6 Reaction of L with 1,2-dichloroethane.

A solution of 0.23 mg (0.5 mmol) of **L** in 5 ml of dry 1,2-dichloroethane (distilled over CaH_2 and stored under nitrogen) was transferred to a gastight gas ampoule and heated at 60 ºC for 32 h to ensure full conversion. After the prescribed time, the ampoule was cooled and a 0.1 ml sample was taken for GC-MS analyses, which showed vinyl chloride as the only volatile product formed in the reaction, as expected for a selective elimination reaction (Scheme S1). The residue was washed with hexane, leaving a pale-yellow solid that was filtered and dried under vacuum. NMR and ESI-MS spectroscopy showed that the solid was pure betaine hydrochloride, H**L**$^+$Cl$^-$. NMR spectra of the cation H**L**$^+$ in CD_2Cl_2 were fully consistent with those of the previously reported tetraphenylborate salt.[2]

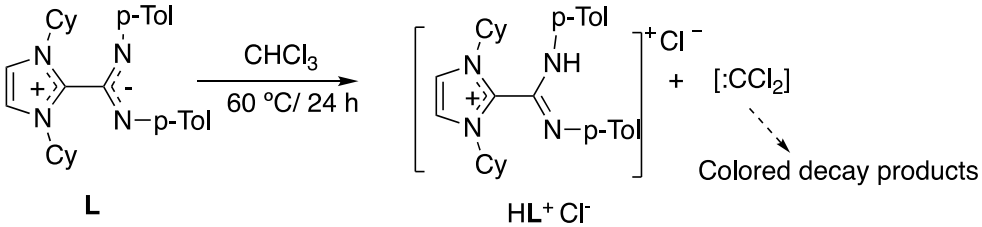


Scheme S1

Spectroscopic data for HL^+ (two geometric isomers in *ca.* 8:1 ratio; only the signals of the major isomer are listed): ^{1}H NMR (400MHz, CD_2Cl_2, 25ºC) δ: 1.09 – 2.01 (overlapping multiplets, 18 H, Cy), 2.27 (s, 3H, *p*-Me), 2.37 (s, 3H, *p*-Me), 2.91 (m, 2H, Cy); 4.13 (m, 2H, 1-CH Cy), 6.52 (d, 2H, $^3J_{HH}$ = 8.0 Hz, CH_{arom}), 7.00 (d, 2H, $^3J_{HH}$ = 8.0 Hz, CH_{arom}), 7.16 (d, 2H, $^3J_{HH}$ = 8.1 Hz, CH_{arom}), 7.28 (s, 2H, Imidz), 7.95 (d, 2H, $^3J_{HH}$ = 8.1 Hz, CH_{arom}), 11.97 (s, HCl); ^{13}C{1H} NMR (100MHz, $CDCl_3$, 25 ºC) δ: 20.7 (*p*-Me), 21.0 (*p*-Me), 24.8 (4-CH_2, Cy), 25.3 (3-CH_2, Cy), 25.3 (3´-CH_2, Cy), 32.9 (2-CH_2, Cy), 33.6 (2´-CH_2, Cy), 59.8 (1-CH, Cy), 119.2 (CH, Imidz), 120.0 (*o*-CH, *p*-Tol), 120.9 (*o*-CH, *p*-Tol), 129.2 (*m*-CH, *p*-Tol), 129.7 (*m*-CH, *p*-Tol), 133.2 (*p*-C, *p*-Tol), 133.5 (*p*-C, *p*-Tol), 137.1 (C, Imidz), 137.2 (*ipso*-C, *p*-Tol), 137.4 (*ipso*-C, *p*-Tol), 145.0 ($C(NAr)_2$). ESI-MS: m/z 455.3 (H**L**$^+$).

7 Reaction of L with Chloroform.

A preliminary study was carried out in $CDCl_3$. To remove any traces of free HCl, the solvent was distilled from CaH_2 prior to use. The solution was monitored at the room temperature. As the reaction advances, an intense red-brown color develops. Within 24 h, about half of the starting betaine had disappeared, and the reaction was complete after heating the same sample for 24 h at 60 ºC. At this point, the protonated betaine HL^+ was the only significant species detected in the ^{1}H NMR, but transient signals were clearly observed at intermediate time. The deep colour is probably due to the decay species of dichlorocarbene, ($:CCl_2$, see Scheme S2) When the mixture was allowed to stand at the room temperature, the betaine hydrochloride crystallized. The crystals were separated from the solution, and the product was characterized by single-crystal X-ray diffraction (see below). The same experiment was repeated in $CHCl_3$. After heating at 60 ºC, the solution was evaporated, taken up in $CDCl_3$ and analysed with ^{1}H NMR and ESI-MS, which showed the signals corresponding to H**L**$^+$, with some baseline noise due to background impurities.



Scheme S2

8 Single-Crystal X-ray Structure Determination for $1{\cdot}ZnCl_4{\cdot}8C_6H_5Br$, $2{\cdot}Zn_2Cl_6{\cdot}3CH_2Cl$, $2{\cdot}Cl{\cdot}13CH_2Cl_2$, and $HLCl{\cdot}3CHCl_3$.

Data collection was performed at 200(2) K, with the crystals covered with perfluorinated ether oil. Single crystals of **$1{\cdot}ZnCl_4{\cdot}8C_6H_5Br$, $2{\cdot}Zn_2Cl_6{\cdot}3CH_2Cl$, $2{\cdot}Cl{\cdot}13CH_2Cl_2$,** and **$HLCl{\cdot}3CHCl_3$.** were mounted on a Bruker-Nonius Kappa CCD single crystal diffractometer equipped with a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Multiscan[3] absorption correction procedures were applied to the data. The structure was solved using the WINGX package,[4] by direct methods (SHELXS-97) and refined using full-matrix least-squares against F^2 (SHELXL-2014/7).[5] All non-hydrogen atoms were anisotropically refined except for some disordered solvent molecules in **2·Cl**. For **$2{\cdot}Zn_2Cl_6$** three dichloromethane molecules crystallized for each unit. Two of them were severely disordered and their contribution from the structure factors was removed with the "squeeze" procedure[6]. For **2·Cl** thirteen molecules of dichloromethane co-crystalized with the compound, three of the molecules showed a positional disorder that was treated, and the atoms for those three molecules were left isotropic except for one atom, C2D. For **$1{\cdot}ZnCl_4$** eight molecules of solvent crystalized with each formula unit of the compound. The "squeeze" procedure was applied to four of them and some restrains were applied to one of the modelled solvent molecules. Finally, **HL^+Cl^-** co-crystallized with three molecules of solvent ($CDCl_3$) and one of them showed some positional disorder that was treated. Hydrogen atoms were geometrically placed and left riding on their parent atoms except for H31, H2 and H41. These were found in the Fourier map and refined freely. Full-matrix least-squares refinements were carried out by minimizing $\sum w(Fo^2 - Fc^2)^2$ with the SHELXL-2014/7 weighting scheme, and stopped when the shift/err ratio was < 0.001. The final residual electron density maps showed no remarkable features. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 1869188 (**$1{\cdot}ZnCl_4{\cdot}8C_6H_5Br$**), 1869189 (**$2{\cdot}Zn_2Cl_6{\cdot}3CH_2Cl$**), 1869190 (**$2{\cdot}Cl{\cdot}13CH_2Cl_2$**) and 1869191 (**$HLCl{\cdot}3CHCl_3$**)

ORTEP drawings for **$1{\cdot}ZnCl_4{\cdot}8C_6H_5Br$, $2{\cdot}Zn_2Cl_6{\cdot}3CH_2Cl$, $2{\cdot}Cl{\cdot}13CH_2Cl_2$,** and **$HLCl{\cdot}3CHCl_3$.** showing relevant intermolecular hydrogen bonds are shown in Figures S3 – S6.

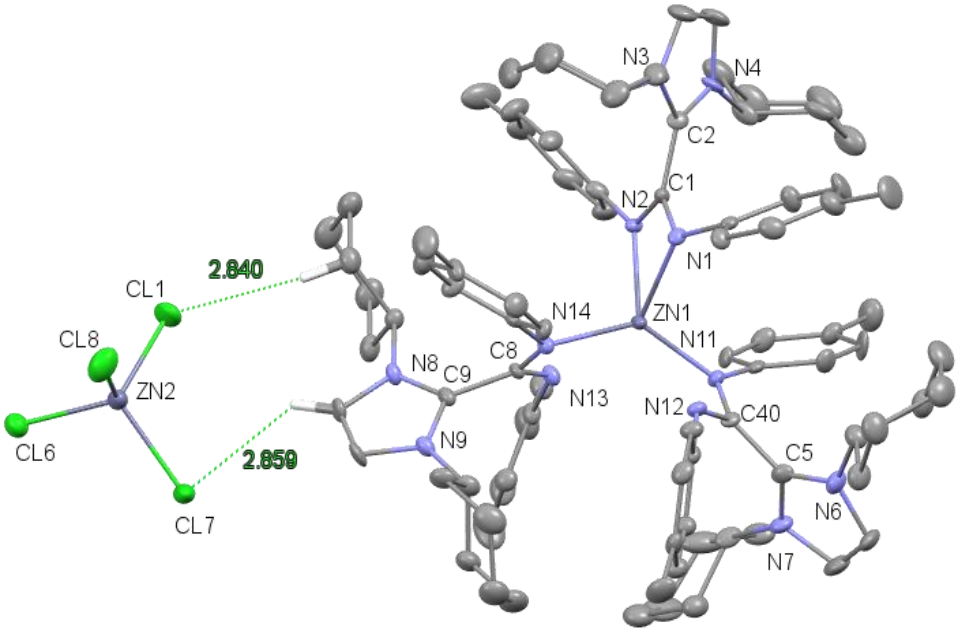


Figure S3. ORTEP view of **1·ZnCl$_4$·8C$_6$H$_5$Br** (ellipsoids at 30% probability) showing intermolecular interactions of the anion with the metal complex.

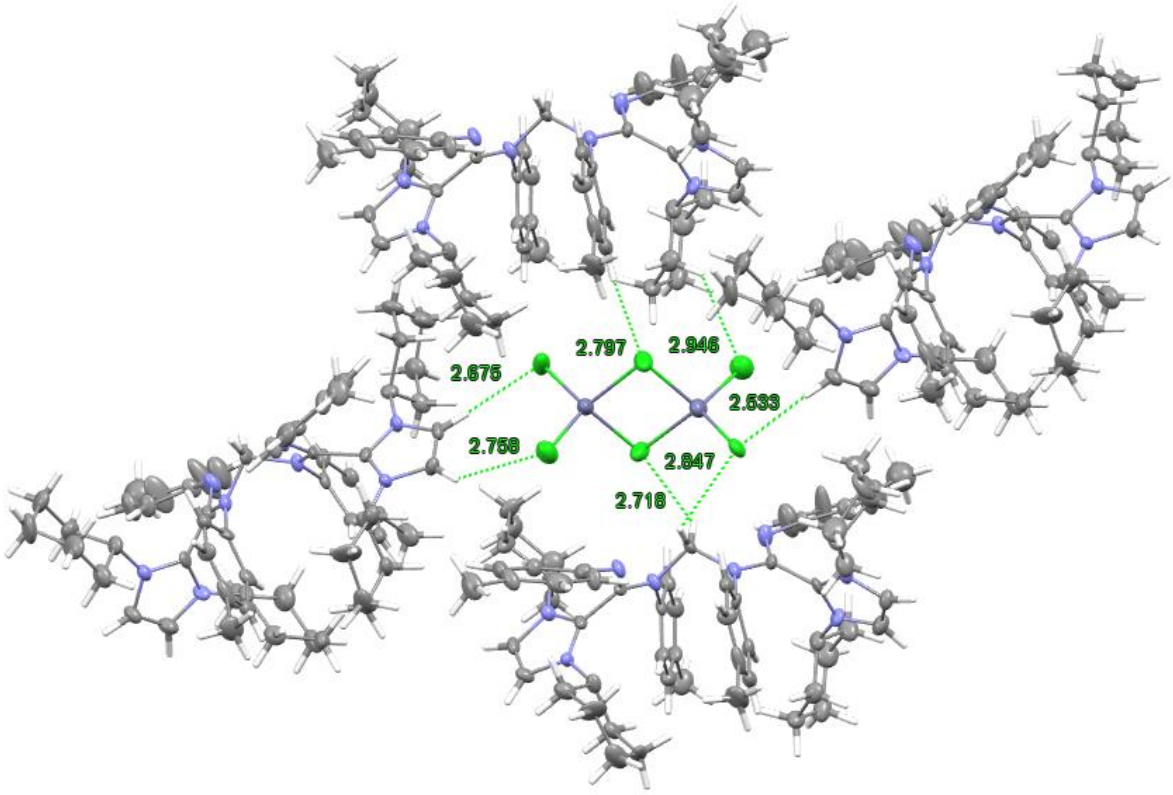


Figure S4. ORTEP view of **2·Zn$_2$Cl$_6$** (ellipsoids at 30% probability) showing intermolecular interactions of the anion with the imidazolium rings.

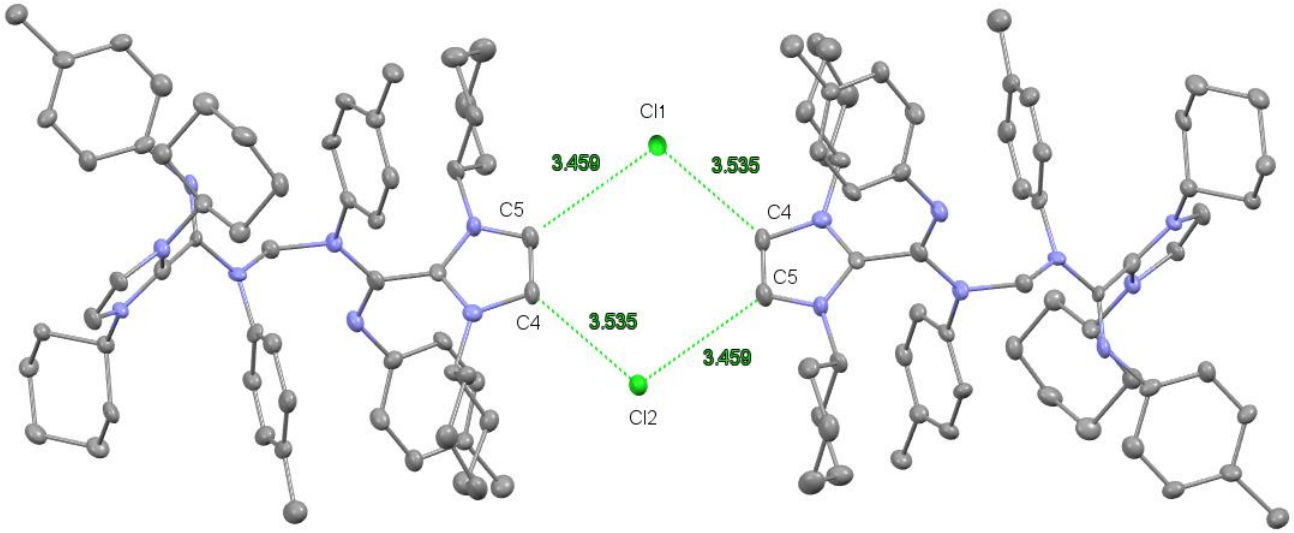


Figure S5. ORTEP view of **2·Cl** (ellipsoids at 30% probability) showing intermolecular interactions of the chloride anions with the imidazolium rings.

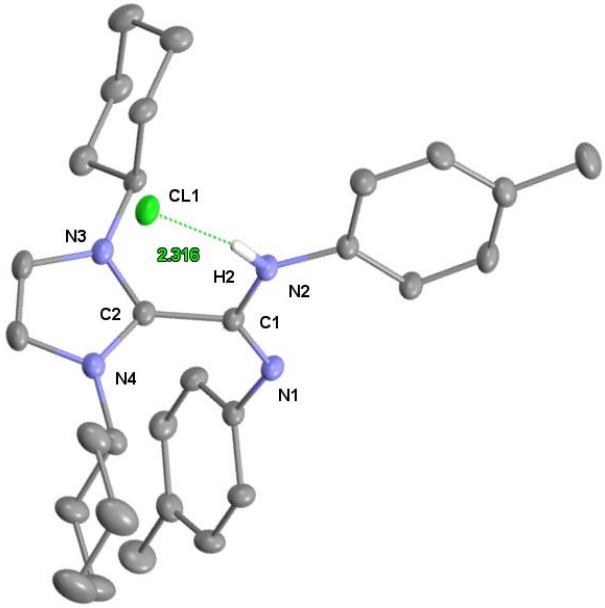


Figure S6. ORTEP view of **HL$^+$Cl$^-$** (ellipsoids at 30% probability) showing the Hydrogen Bonding between the chloride anion and the NH group.

Table S1 Crystallographic data for **1·$ZnCl_4$·$8C_6H_5Br$, 2·Zn_2Cl_6·$3CH_2Cl$, 2·Cl·$13CH_2Cl_2$, and HLCl·$3CHCl_3$.**

	1·$ZnCl_4$·$8C_6H_5Br$	**2·Zn_2Cl_6·$3CH_2Cl_2$**	**2·Cl·$13CH_2Cl_2$**	**HLCl·$3CHCl_3$**
Empirical formula	$C_{98}H_{108}Cl_4N_{12}Zn_2$· $C_{48}H_{40}Br_8$	$C_{61}H_{74}Cl_6N_8Zn_2$· $C_3H_6Cl_6$	$C_{61}H_{76}Cl_2N_8$· $C_{13}H_{26}Cl_{26}$	$C_{30}H_{39}ClN_4$· $C_3H_3Cl_9$
Formula weight	2886.50	1517.50	2096.23	849.20
Color	Yellow	Yellow	Yellow	Light yellow
Crystal size (mm)	0.51 0.48 0.48	0.39 0.30 0.15	0.49 0.48 0.28	0.48 0.41 0.36
Crystal system	Triclinic,	Orthorhombic	Triclinic,	Monoclinic
Space group	*P-1*	*Pbca*	*P-1*	*C 2/c*
a (Å)	17.6822(15)	21.712(2)	12.838(6) A	16.0787(16)
b (Å)	17.7483(17)	13.037(2)	15.476(15) A	21.553(3)
c (Å)	25.194(3)	54.215(14)	27.491(9)	24.176(3)
α (°)	78.121(7)	90	98.93(4)	90
β (°)	77.607(10)	90	92.92(3)	94.498(9)
γ (°)	60.899(8)	90	110.32(5)	90
V (Å^3)	6699.7(13)	15346(5)	5028(6)	8352.1(19)
Z	2	8	2	8
$\rho_{calcd.}$ (mg m^{-3})	1.431	1.314	1.385	1.351
F_{000}	2936	6272	2156	3504
μ (mm^{-1})	2.876	1.084	0.798	0.696
θ Range (°)	3.043 to 24.787	3.006 to 23.707	3.020 to 23.200	3.073 to 25.000
Reflns. Collected	36738	59272	26278	26951
Indep. Reflns./R(int)	21472 / 0.0719	11612 / 0.1419	14192 / 0.1069	7326 / 0.0450
Data/restraints/param	21472 / 42 / 1225	11612 / 0 / 721	14192 / 0 / 986	7326 / 0 / 446
R_1/wR_2 (I > 2σ(I)) [a]	0.0739 / 0.1788	0.0848 / 0.2178	0.0940 / 0.2284	0.0677 / 0.1865
R_1/wR_2 (all data)[a]	0.1554 / 0.2083	0.1887 / 0.2526	0.1980 / 0.2905	0.0886 / 0.1988
GOF	0.856	0.981	0.919	1.086
Max/min $\Delta\rho$ (e.Å^{-3})	0.694 / -0.783	0.545 / -0.395	0.957 / -0.694	0.983 / -0.717

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$

Table S2. Selected bond lengths (Å) and angles (°) for **1·ZnCl$_4$·8C$_6$H$_5$Br**

Bond lengths (Å)			
Zn(1)-N(14)	1.972(5)	N(7)-C(5)	1.348(7)
Zn(1)-N(11)	1.969(4)	N(7)-C(6)	1.387(8)
Zn(1)-N(1)	2.119(5)	N(7)-C(71)	1.491(8)
Zn(1)-N(2)	2.150(5)	N(8)-C(9)	1.344(7)
Zn(1)-C(1)	2.514(5)	N(8)-C(20)	1.377(8)
Zn(2)-Cl(1)	2.253(2)	N(8)-C(81)	1.484(7)
Zn(2)-Cl(7)	2.2678(19)	N(9)-C(10)	1.374(8)
Zn(2)-Cl(8)	2.275(2)	N(9)-C(9)	1.357(7)
Zn(2)-Cl(6)	2.274(2)	N(9)-C(91)	1.469(8)
N(1)-C(1)	1.325(7)	N(11)-C(40)	1.332(7)
N(1)-C(11)	1.416(7)	N(11)-C(110)	1.410(7)
N(2)-C(1)	1.314(7)	N(12)-C(40)	1.310(7)
N(2)-C(21)	1.404(7)	N(12)-C(120)	1.417(7)
N(3)-C(2)	1.326(7)	N(13)-C(8)	1.304(7)
N(3)-C(3)	1.393(8)	N(13)-C(130)	1.414(8)
N(3)-C(31)	1.482(8)	N(14)-C(8)	1.328(7)
N(4)-C(2)	1.358(7)	N(14)-C(140)	1.402(7)
N(4)-C(4)	1.378(8)	C(1)-C(2)	1.505(8)
N(4)-C(41)	1.478(8)	C(3)-C(4)	1.300(10)
N(6)-C(5)	1.316(8)	C(5)-C(40)	1.494(8)
N(6)-C(7)	1.372(8)	C(6)-C(7)	1.321(10)
N(6)-C(61)	1.470(8)	C(8)-C(9)	1.494(8)
Angles (°)			
N(14)-Zn(1)-N(11)	132.27(19)	N(2)-C(1)-Zn(1)	58.8(3)
N(14)-Zn(1)-N(1)	114.75(19)	N(1)-C(1)-Zn(1)	57.4(3)
N(11)-Zn(1)-N(1)	106.56(19)	C(2)-C(1)-Zn(1)	178.6(4)
N(14)-Zn(1)-N(2)	105.03(18)	N(4)-C(2)-N(3)	108.4(5)
N(11)-Zn(1)-N(2)	114.43(19)	N(4)-C(2)-C(1)	126.1(5)
N(1)-Zn(1)-N(2)	63.30(17)	N(3)-C(2)-C(1)	125.4(5)
N(14)-Zn(1)-C(1)	113.71(18)	C(4)-C(3)-N(3)	109.9(6)
N(11)-Zn(1)-C(1)	113.98(19)	C(3)-C(4)-N(4)	107.0(6)
N(1)-Zn(1)-C(1)	31.80(18)	N(6)-C(5)-N(7)	108.2(5)
N(2)-Zn(1)-C(1)	31.50(18)	N(6)-C(5)-C(40)	128.3(6)
Cl(1)-Zn(2)-Cl(7)	109.61(8)	N(7)-C(5)-C(40)	123.5(5)
Cl(1)-Zn(2)-Cl(8)	108.13(10)	C(7)-C(6)-N(7)	108.1(6)

Cl(7)-Zn(2)-Cl(8)	108.73(9)	C(6)-C(7)-N(6)	107.2(6)
Cl(1)-Zn(2)-Cl(6)	111.67(8)	N(13)-C(8)-N(14)	118.8(5)
Cl(7)-Zn(2)-Cl(6)	110.28(8)	N(13)-C(8)-C(9)	122.1(5)
Cl(8)-Zn(2)-Cl(6)	108.35(8)	N(14)-C(8)-C(9)	119.1(5)
C(1)-N(1)-C(11)	123.6(5)	N(8)-C(9)-N(9)	108.1(5)
C(1)-N(1)-Zn(1)	90.8(3)	N(8)-C(9)-C(8)	126.7(5)
C(11)-N(1)-Zn(1)	137.3(3)	N(9)-C(9)-C(8)	125.2(5)
C(1)-N(2)-C(21)	124.5(5)	N(9)-C(10)-C(20)	107.4(5)
C(1)-N(2)-Zn(1)	89.7(3)	C(17)-C(11)-N(1)	119.2(5)
C(21)-N(2)-Zn(1)	141.0(4)	C(12)-C(11)-N(1)	121.8(5)
C(2)-N(3)-C(3)	106.6(6)	C(10)-C(20)-N(8)	107.6(5)
C(2)-N(3)-C(31)	128.0(5)	C(27)-C(21)-N(2)	123.5(5)
C(3)-N(3)-C(31)	125.4(6)	C(27)-C(21)-C(22)	120.0(5)
C(2)-N(4)-C(4)	108.1(5)	N(2)-C(21)-C(22)	116.5(5)
C(2)-N(4)-C(41)	126.6(5)	C(36)-C(31)-N(3)	110.9(5)
C(4)-N(4)-C(41)	125.4(5)	C(36)-C(31)-C(32)	110.8(5)
C(5)-N(6)-C(7)	109.4(6)	N(3)-C(31)-C(32)	111.1(5)
C(5)-N(6)-C(61)	125.3(5)	N(12)-C(40)-N(11)	116.4(5)
C(7)-N(6)-C(61)	125.3(6)	N(12)-C(40)-C(5)	121.9(5)
C(5)-N(7)-C(6)	107.1(5)	N(11)-C(40)-C(5)	121.6(5)
C(5)-N(7)-C(71)	126.7(5)	N(4)-C(41)-C(46)	110.9(5)
C(6)-N(7)-C(71)	126.0(5)	N(4)-C(41)-C(42)	108.2(6)
C(9)-N(8)-C(20)	108.5(5)	N(6)-C(61)-C(62)	111.1(6)
C(9)-N(8)-C(81)	126.5(5)	N(6)-C(61)-C(66)	111.1(5)
C(20)-N(8)-C(81)	125.0(5)	C(76)-C(71)-N(7)	111.4(5)
C(10)-N(9)-C(9)	108.4(5)	C(76)-C(71)-C(72)	110.3(6)
C(10)-N(9)-C(91)	125.5(5)	N(7)-C(71)-C(72)	108.8(6)
C(9)-N(9)-C(91)	126.1(5)	N(8)-C(81)-C(86)	109.4(5)
C(40)-N(11)-C(110)	126.7(5)	N(8)-C(81)-C(82)	110.2(5)
C(40)-N(11)-Zn(1)	108.0(4)	N(9)-C(91)-C(96)	111.6(5)
C(110)-N(11)-Zn(1)	123.9(3)	N(9)-C(91)-C(92)	109.7(5)
C(40)-N(12)-C(120)	124.6(5)	C(115)-C(110)-N(11)	117.9(5)
C(8)-N(13)-C(130)	124.5(5)	C(111)-C(110)-N(11)	123.4(5)
C(8)-N(14)-C(140)	126.1(5)	C(121)-C(120)-N(12)	122.5(5)
C(8)-N(14)-Zn(1)	108.9(4)	N(12)-C(120)-C(125)	118.4(5)
C(140)-N(14)-Zn(1)	122.9(4)	C(135)-C(130)-N(13)	123.8(6)
N(2)-C(1)-N(1)	116.2(5)	C(131)-C(130)-N(13)	118.4(6)

N(2)-C(1)-C(2)	122.6(5)	C(141)-C(140)-N(14)	117.6(5)
N(1)-C(1)-C(2)	121.2(5)	C(145)-C(140)-N(14)	124.1(5)

Table S3. Selected bond lengths (Å) and angles (°) for **2·Zn_2Cl_6·$3CH_2Cl_2$**

Bond lengths (Å)		**Angles (°)**	
Zn(1)-Cl(8)	2.190(3)	N(4)-C(7)	1.331(9)
Zn(1)-Cl(3)	2.223(3)	N(4)-C(8)	1.349(10)
Zn(1)-Cl(5)	2.348(2)	N(4)-C(41)	1.486(10)
Zn(1)-Cl(7)	2.351(3)	N(5)-C(3)	1.358(9)
Zn(2)-Cl(6)	2.194(3)	N(5)-C(51)	1.420(9)
Zn(2)-Cl(4)	2.209(3)	N(5)-C(1)	1.493(9)
Zn(2)-Cl(7)	2.333(3)	N(6)-C(3)	1.293(9)
Zn(2)-Cl(5)	2.359(3)	N(6)-C(61)	1.411(10)
N(1)-C(4)	1.340(9)	N(7)-C(71)	1.389(10)
N(1)-C(6)	1.373(9)	N(7)-C(2)	1.417(9)
N(1)-C(11)	1.484(10)	N(7)-C(1)	1.458(9)
N(2)-C(4)	1.342(9)	N(8)-C(2)	1.288(9)
N(2)-C(5)	1.376(9)	N(8)-C(81)	1.417(10)
N(2)-C(21)	1.488(10)	C(2)-C(7)	1.489(10)
N(3)-C(7)	1.346(9)	C(3)-C(4)	1.516(10)
N(3)-C(9)	1.359(10)	C(5)-C(6)	1.324(10)
N(3)-C(31)	1.454(10)	C(8)-C(9)	1.362(11)
Angles (°)			
Cl(8)-Zn(1)-Cl(3)	116.32(10)	C(3)-N(6)-C(61)	125.9(7)
Cl(8)-Zn(1)-Cl(5)	111.87(12)	C(71)-N(7)-C(2)	124.7(7)
Cl(3)-Zn(1)-Cl(5)	113.78(10)	C(71)-N(7)-C(1)	118.6(6)
Cl(8)-Zn(1)-Cl(7)	112.76(12)	C(2)-N(7)-C(1)	116.6(7)
Cl(3)-Zn(1)-Cl(7)	106.69(11)	C(2)-N(8)-C(81)	123.2(7)
Cl(5)-Zn(1)-Cl(7)	92.92(9)	N(7)-C(1)-N(5)	108.4(6)
Cl(6)-Zn(2)-Cl(4)	115.45(11)	N(8)-C(2)-N(7)	120.2(7)
Cl(6)-Zn(2)-Cl(7)	113.97(12)	N(8)-C(2)-C(7)	125.0(7)
Cl(4)-Zn(2)-Cl(7)	111.12(11)	N(7)-C(2)-C(7)	114.8(7)
Cl(6)-Zn(2)-Cl(5)	109.25(12)	N(5)-C(3)-N(6)	122.3(7)

Cl(4)-Zn(2)-Cl(5)	111.78(12)	N(5)-C(3)-C(4)	116.8(7)
Cl(7)-Zn(2)-Cl(5)	93.12(9)	N(6)-C(3)-C(4)	120.9(7)
Zn(1)-Cl(5)-Zn(2)	86.68(9)	N(1)-C(4)-N(2)	109.1(6)
Zn(2)-Cl(7)-Zn(1)	87.20(9)	N(1)-C(4)-C(3)	123.9(7)
C(4)-N(1)-C(6)	107.0(6)	N(2)-C(4)-C(3)	125.6(7)
C(4)-N(1)-C(11)	126.7(6)	C(6)-C(5)-N(2)	107.8(7)
C(6)-N(1)-C(11)	126.0(7)	C(5)-C(6)-N(1)	108.7(7)
C(4)-N(2)-C(5)	107.4(6)	N(3)-C(7)-N(4)	108.4(7)
C(4)-N(2)-C(21)	126.5(7)	N(3)-C(7)-C(2)	126.9(8)
C(5)-N(2)-C(21)	126.1(7)	N(4)-C(7)-C(2)	123.7(7)
C(7)-N(3)-C(9)	108.1(7)	C(9)-C(8)-N(4)	107.7(8)
C(7)-N(3)-C(31)	125.4(7)	C(8)-C(9)-N(3)	107.1(8)
C(9)-N(3)-C(31)	126.5(7)	N(1)-C(11)-C(16)	110.3(7)
C(7)-N(4)-C(8)	108.7(7)	N(1)-C(11)-C(12)	110.7(7)
C(7)-N(4)-C(41)	127.8(7)	N(2)-C(21)-C(26)	108.2(7)
C(8)-N(4)-C(41)	123.5(7)	N(2)-C(21)-C(22)	109.9(7)
C(3)-N(5)-C(51)	125.0(6)	N(3)-C(31)-C(32)	110.6(7)
C(3)-N(5)-C(1)	117.3(6)	N(3)-C(31)-C(36)	107.9(7)
C(51)-N(5)-C(1)	117.4(6)	N(4)-C(41)-C(46)	108.7(7)
		N(4)-C(41)-C(42)	111.5(7)

Table S4. Selected bond lengths (Å) and angles (°) for **2·Cl_2·13CH_2Cl_2**

Bond lengths (Å)			
N(1)-C(2)	1.379(10)	N(5)-C(1)	1.471(10)
N(1)-C(11)	1.419(10)	N(6)-C(6)	1.267(10)
N(1)-C(1)	1.458(10)	N(6)-C(61)	1.411(10)
N(2)-C(2)	1.275(9)	N(7)-C(7)	1.347(9)
N(2)-C(21)	1.407(10)	N(7)-C(9)	1.410(10)
N(3)-C(3)	1.326(10)	N(7)-C(71)	1.473(10)
N(3)-C(5)	1.377(10)	N(8)-C(7)	1.300(10)
N(3)-C(31)	1.466(11)	N(8)-C(8)	1.390(10)
N(4)-C(3)	1.329(10)	N(8)-C(81)	1.486(10)
N(4)-C(4)	1.384(10)	C(2)-C(3)	1.499(11)
N(4)-C(41)	1.492(10)	C(4)-C(5)	1.343(11)
N(5)-C(6)	1.394(10)	C(6)-C(7)	1.525(12)
		C(8)-C(9)	1.344(11)

N(5)-C(51)	1.409(10)		
Angles (°)			
C(2)-N(1)-C(11)	125.6(6)	N(1)-C(2)-C(3)	115.8(7)
C(2)-N(1)-C(1)	117.4(6)	N(4)-C(3)-N(3)	107.4(7)
C(11)-N(1)-C(1)	116.7(6)	N(4)-C(3)-C(2)	126.0(7)
C(2)-N(2)-C(21)	123.7(7)	N(3)-C(3)-C(2)	126.2(8)
C(3)-N(3)-C(5)	109.4(7)	C(5)-C(4)-N(4)	106.4(7)
C(3)-N(3)-C(31)	128.2(7)	C(4)-C(5)-N(3)	107.2(7)
C(5)-N(3)-C(31)	122.4(7)	N(6)-C(6)-N(5)	120.6(7)
C(3)-N(4)-C(4)	109.6(7)	N(6)-C(6)-C(7)	124.4(7)
C(3)-N(4)-C(41)	128.1(7)	N(5)-C(6)-C(7)	115.0(8)
C(4)-N(4)-C(41)	122.4(7)	N(8)-C(7)-N(7)	110.4(7)
C(6)-N(5)-C(51)	124.1(7)	N(8)-C(7)-C(6)	126.5(7)
C(6)-N(5)-C(1)	118.2(7)	N(7)-C(7)-C(6)	122.0(7)
C(51)-N(5)-C(1)	117.5(6)	C(9)-C(8)-N(8)	107.7(7)
C(6)-N(6)-C(61)	125.3(7)	C(8)-C(9)-N(7)	106.8(7)
C(7)-N(7)-C(9)	106.6(6)	N(3)-C(31)-C(36)	111.4(7)
C(7)-N(7)-C(71)	130.1(6)	N(3)-C(31)-C(32)	111.9(7)
C(9)-N(7)-C(71)	123.1(7)	N(4)-C(41)-C(46)	110.4(6)
C(7)-N(8)-C(8)	108.5(7)	N(4)-C(41)-C(42)	109.0(7)
C(7)-N(8)-C(81)	129.1(7)	N(7)-C(71)-C(76)	109.8(6)
C(8)-N(8)-C(81)	122.4(7)	N(7)-C(71)-C(72)	110.7(7)
N(1)-C(1)-N(5)	109.7(6)	N(8)-C(81)-C(82)	113.2(6)
N(2)-C(2)-N(1)	120.1(7)	N(8)-C(81)-C(86)	110.0(7)
N(2)-C(2)-C(3)	124.0(7)		

Table S5. Selected bond lengths (Å) and angles (°) for **HLCl·3CHCl$_3$**

Bond lengths (Å)			
N(1)-C(1)	1.280(4)	N(3)-C(31)	1.484(4)
N(1)-C(11)	1.417(4)	N(4)-C(2)	1.332(4)
N(2)-C(1)	1.355(4)	N(4)-C(3)	1.376(4)
N(2)-C(21)	1.408(4)	N(4)-C(41)	1.481(5)
N(3)-C(2)	1.342(4)	C(1)-C(2)	1.498(4)
N(3)-C(4)	1.378(4)	C(3)-C(4)	1.344(5)
Angles (°)			

C(1)-N(1)-C(11)	120.8(3)	N(3)-C(2)-C(1)	125.0(3)
C(1)-N(2)-C(21)	129.2(3)	C(4)-C(3)-N(4)	107.8(3)
C(2)-N(3)-C(4)	108.3(3)	C(3)-C(4)-N(3)	107.1(3)
C(2)-N(3)-C(31)	126.5(3)	C(12)-C(11)-N(1)	122.2(3)
C(4)-N(3)-C(31)	125.3(3)	C(16)-C(11)-N(1)	118.8(3)
C(2)-N(4)-C(3)	108.3(3)	C(13)-C(12)-C(11)	120.3(3)
C(2)-N(4)-C(41)	126.9(3)	C(22)-C(21)-N(2)	124.7(3)
C(3)-N(4)-C(41)	124.7(3)	C(26)-C(21)-N(2)	116.2(3)
N(1)-C(1)-N(2)	124.5(3)	N(3)-C(31)-C(36)	111.3(3)
N(1)-C(1)-C(2)	124.1(3)	N(3)-C(31)-C(32)	110.0(3)
N(2)-C(1)-C(2)	111.4(3)	N(4)-C(41)-C(46)	110.5(3)
N(4)-C(2)-N(3)	108.5(3)	N(4)-C(41)-C(42)	110.1(3)
N(4)-C(2)-C(1)	126.5(3)		

9 Computational Details

DFT Methods: All calculations were performed with the Spartan '16 software package.[7] The structures of the molecules involved in the theoretical model (intermediates and transition states) were optimized using the GGA functional PBE, the 6-31G* basis set and the standard solvent model CPCM implemented by default in Spartan, for dichloromethane, setting the energy gradient tolerance to 5 x 10^{-5}. Vibrational calculations were carried out in each case to check that every optimized structure corresponds to a minimum in the Potential Energy Surface. We have found that this method combination provides molecular geometries at a fraction of the computation time used by standard hybrid functionals, like B3LYP.[8] In addition, the PBE functional provides a good account of the vibrational frequencies, that is expected to translate in a good estimation of the zero-point energy (ZPE) and thermodynamic corrections, TC(T), used to compute Gibbs energies. The latter were computed at 1 bar and two different temperatures: 298.15 K for standard values and 333.15 K. The electronic contribution to the energy was further refined performing a single-point calculation with the RSH-GGA functional ωB97X-D (that also includes an empirical correction for the dispersion forces) and the triple-ζ basis set 6-311++G**. The latter calculations were accelerated with the "*double basis set*" option available in Spartan, in which SCF convergence is achieved first at the 6-311G* level, and then corrected perturbatively for the effect of the basis extension.[9] For the calculation of free energies, we computed the thermal energy correction (TC(T)) from the PBE/6-31G* model (Eq. S3). Since it is known that implicit solvent models give better results with small basis functions, we also computed a solvent correction (E_{CPCM}) from the PBE/6-31G* calculation, rather than including the solvent correction in the high-level calculation. To this end, a single point energy calculation was carried out over the optimized structure using the same PBE/6-31G* model in the gas phase (*i. e.*, no CPCM model applied), and then we obtained the difference with value for solvent-corrected energy (Eq S4).The final energies E (SCF+ZPE) and free energies (G^o) computed for each species were obtained adding the high-level single-point electronic energy ($E_{3\zeta}$) to the ZPE or TC(T) and solvent corrections deduced from the PBE 6-31G* corrections (Eqs. S5 and S6).

$$TC(T) = G_T^o - E(SCF) \text{ at the PBE/CPCM/6-31G* level} \quad \text{(S3)}$$

$$E_{CPCM} = E(SCF)_{opt,solvent} - E(SCF)_{SP,gas} \text{ at the PBE/6-31G* level} \quad \text{(S4)}$$

$$E = E_{3z}^{\omega B97X-D} + ZPE_{2z}^{PBE} + E_{CPCM} \quad \text{(S5)}$$

$$G_T^0 = E_{3z}^{\omega B97X-D} + TC(T) + E_{CPCM} \quad \text{(S6)}$$

Theoretical Model: In order to reduce the number of atoms in the system, we introduced two structural simplifications in the betaine molecule: i) cyclohexyl groups attached to the imidazolium

unit were replaced with methyl, and ii) *p*-tolyl aromatic groups attached to the amidinate unit have been replaced with simpler phenyl rings. As the cyclohexyl groups are removed from the reactive amidinate, and the phenyl and *p*-tolyl fragments have very similar sizes, we believe that the resulting model (***L***) should be nearly equivalent to the real molecule **L** in terms of steric hindrance. On the other hand, the electronic effect of the replacement of *p*-methyl by hydrogen at the amidinate unit is small. Chemical formulae describing the meaning of the codes are shown in Figure S7.

Ionic compounds with a small-sized anion such as chloride in a relatively low-polarity solvent such as dichloromethane are likely to form ion pairs. Formation of such ion pairs could have a strong influence on the relative energies of intermediates and transition states. Thus, we have modelled intimate ion pairs both for singly and for doubly charged species; in the latter cases, in addition to the ternary, electroneutral ion pairs with full charge cancellation, we considered singly charged, binary ion pairs. Ion pairs were built by placing the chloride anion or anions at a long distance from the cation and allowing the minimizer to run until the convergence criteria were fulfilled. This method may afford local rather than absolute minima, but provides a hint on the effect of ion-pair association. In all cases but one (for the cylic species $[c\text{-}L CH_2]^{2+}$), inclusion of thermal corrections leads to more favourable ΔG changes for the fully ion separated species. Therefore, we have not included such ion pairs in the main text body, but we kept the computed data in thee SI material. Cartesian coordinates for each of the optimized structures are provided in the last section of this file.

In order to calculate the relative energy at each of the steps of the double substitution process, we have set the reference energy as that of the combined reactants (*i. e.* 2 ***L*** + CH_2Cl_2). For each individual species, the relative energies were computed as the sum of that of the species considered and those of the species not explicitly considered that are necessary to preserve stoichiometry, minus the reference value. **Tables S6 and S7** provide absolute and corrected electronic energies for each of the species involved in the model. These are graphically illustrated in the energy diagram provided in Figure S8. **Table S8** lists atomic coordinates for all optimized geometries.

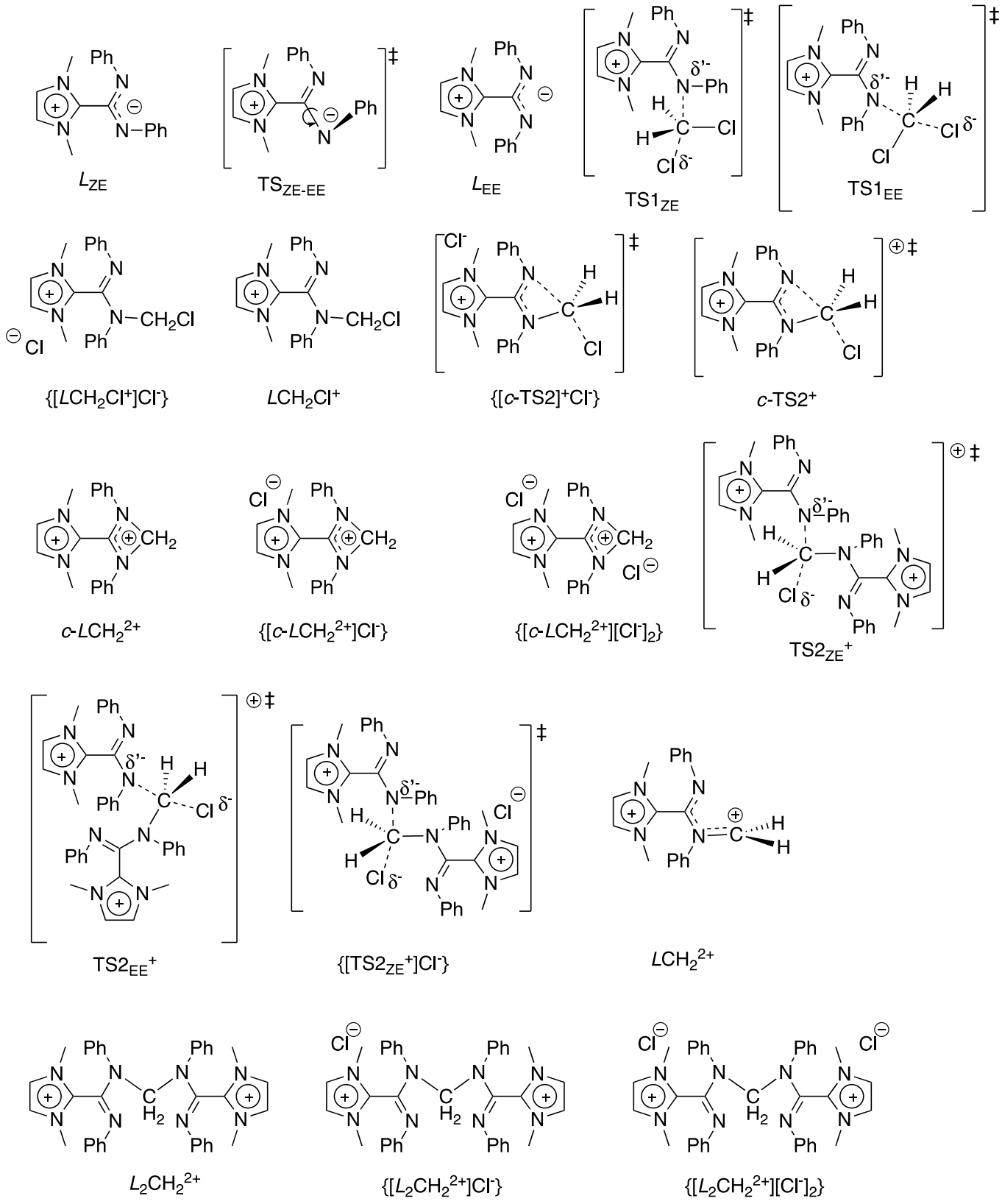


Figure S7 Molecular formulae and symbolic representation of modelled intermediates and transition states.

Table S6 Computed energies, thermal and solvent and correction factors (Kcal·mol^{-1})

Molecule	Optimization level: PBE-CPCM/6-31G*. solvent = CH_2Cl_2						Single point (SP) PBE/6-31G*. gas		SP ωB97X-D/ 6-311++G**. gas
	$E_{opt.solv}$	ZPE	G^o_{298K}	TC_{298}	G^o_{333K}	TC_{333K}	$E_{SP.gas}$	E_{CPCM}	$E_{SP.gas}$
L_{ZE}	-573906.77	200.42	-573738.94	167.84	-573744.68	162.10	-574563.24	-16.45	-574563.24
CH_2Cl_2	-601930.50	18.12	-601928.83	1.67	-601931.14	-0.64	-602231.82	-3.078	-602231.82
TS_{ZE-EE}	-573891.93	199.61	-573723.65	168.28	-573729.21	162.72	-574546.91	-18.54	-574546.91
L_{EE}	-573900.12	199.87	-573733.11	167.01	-573738.90	161.22	-574558.87	-19.30	-574558.87
$TS1_{ZE}$	-1175814.67	218.58	-1175634.80	179.87	-1175641.76	172.91	-1176773.47	-25.33	-1176773.47
$TS1_{EE}$	-1175810.36	218.49	-1175630.63	179.73	-1175637.57	172.79	-1176769.31	-28.86	-1176769.31
$\{[LCH_2Cl^+]Cl^-\}$	-1175854.75	220.69	-1175670.96	183.79	-1175677.63	177.12	-1176823.09	-34.04	-1176823.09
LCH_2Cl^+	-887081.73	220.89	-886896.09	185.64	-886902.40	179.34	-887906.70	-42.600	-887906.70
Cl^-	-288680.78	0.00	-288690.81	-10.03	-288692.17	-11.39	-288831.30	-67.64	-288831.30
$\{[c\text{-}TS2]^+Cl^-\}$	-1175815.93	219.45	-1175633.84	182.09	-1175640.63	175.30	-1176773.76	-45.24	-1176773.76
$c\text{-}TS2^+$	-887034.14	219.09	-886850.10	184.04	-886856.41	177.74	-887848.12	-59.027	-887848.12
$\{[c\text{-}LCH_2^{2+}]Cl^-\}$	-887050.63	220.30	-886866.48	184.15	-886872.94	177.69	-887864.03	-67.78	-887864.03
$\{[c\text{-}LCH_2^{2+}][Cl^-]_2\}$	-1175838.98	220.53	-1175657.09	181.89	-1175664.05	174.93	-1176808.13	-45.78	-1176808.13
$c\text{-}LCH_2^{2+}$	-598205.63	219.85	-598020.53	185.09	-598026.64	178.98	-598884.51	-137.17	-598884.51
$\{[TS2_{EE}^+]Cl^-\}$	-1749755.86	421.34	-1749392.10	363.76	-1749403.24	352.62	-1751393.60	-52.60	-1751393.60
$TS2_{EE}^+$	-1460989.48	421.16	-1460623.31	366.17	-1460633.95	355.53	-1462480.31	-56.94	-1462480.31
$\{[TS2_{ZE}^+]Cl^-\}]$	-1749805.46	423.70	-1749429.25	376.21	-1749438.72	366.74	-1751390.19	-49.21	-1751390.19
$TS2_{ZE}^+$	-1460993.43	421.68	-1460625.56	367.87	-1460636.05	357.38	-1462484.41	-53.46	-1462484.41
$L_2CH_2^{2+}$	-1172194.55	423.23	-1171824.14	370.41	-1171834.34	360.21	-1173738.59	-115.32	-1173738.59
$\{[L_2CH_2^{2+}][Cl^-]_2\}$	-1749775.17	423.14	-1749409.27	365.90	-1749420.36	354.81	-1751422.10	-69.20	-1751422.10
$\{[L_2CH_2^{2+}]Cl^-\}$	-1461014.22	423.68	-1460643.32	370.90	-1460653.66	360.56	-1462515.47	-69.41	-1462515.47
LCH_2^{2+}	-598195.34	218.93	-598010.33	185.01	-598.02	178.98	-598873.42	-135.17	-598873.42

Table S7 Final composed ΔE(SCF+ZPE) and ΔG° (at 298 and 333 K) computed at the PBE-CPCM/6-31G*//ωB97X-D/6-311++G** level (Eqs S5 and S6) for the species and transition states involved in the model relative to the reactants (all values in Kcal·mol^{-1})

Molecular Components	ΔE	ΔG^{o}_{298K}	ΔG^{o}_{333K}
2 $\boldsymbol{L_{ZE}}$ + CH_2Cl_2	0.0	0.0	0.0
$\mathbf{TS_{ZE\text{-}EE}}$ + L_{ZE} + CH_2Cl_2	14.3	15.8	16.0
$\boldsymbol{L_{EE}}$ + L_{ZE} + CH_2Cl_2	1.8	2.5	2.5
$\mathbf{TS1_{ZE}}$ + L_{ZE}	16.5	31.5	33.3
$\mathbf{TS1_{EE}}$ + L_{ZE}	14.5	28.0	29.7
$\{[LCH_2Cl^+]Cl^-\}$ + L_{ZE}	-36.9	-21.4	-19.5
LCH_2Cl^+ + Cl^- + L_{ZE}	-31.5	-26.7	-26.2
$\{[c\text{-}TS2]^+Cl^-\}$ + L_{ZE}	1.1	15.6	17.4
$c\text{-}TS2^+$ + Cl^- + L_{ZE}	7.4	12.0	12.5
$\{[c\text{-}LCH_2^{2+}]Cl^-\}^+$ + Cl^- + L_{ZE}	-9.2	-4.5	-4.0
$\{[c\text{-}LCH_2^{2+}][Cl^-]_2\}$ + L_{ZE}	-27.6	-11.3	-9.2
$c\text{-}LCH_2^{2+}$ + 2 Cl^- + L_{ZE}	-2.7	-5.8	-6.2
$\{[TS2_{EE}^+]Cl^-\}$	-42.9	-8.5	-4.1
$TS2_{EE}^+$ + Cl^-	-35.7	-11.5	-8.6
$\{[TS2_{ZE}^+]Cl^-\}$	-42.2	-8.9	-4.7
$TS2_{ZE}^+$ + Cl^-	-35.7	-11.7	-8.8
$\{[L_2CH_2^{2+}][Cl^-]_2\}$	-82.0	-46.6	-42.1
$\{[L_2CH_2^{2+}]Cl^-\}$ + Cl^-	-75.7	-49.7	-46.4
Ure	-66.0	-50.3	-48.4
LCH_2^{2+} + 2 Cl^- + L_{ZE}	3.4	0.9	0.5

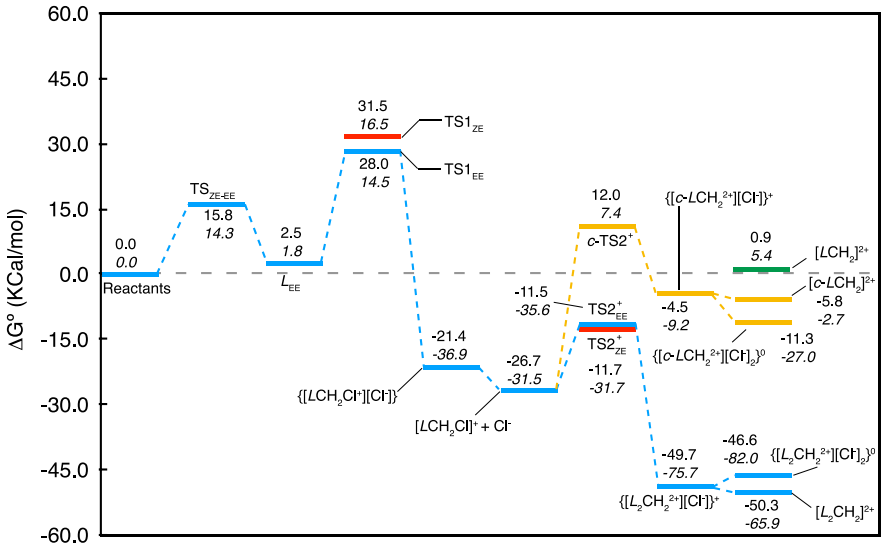


Figure S8. Energy diagram showing free energies (ΔG°) and ZPE-corrected SCF energies (E+ ZPE, italics) relative to the reactants (2 $\boldsymbol{L_{ZE}}$ + 2 CH_2Cl_2).

Table S8. Atomic cartesian coordinates (xyz) for all optimized molecular geometries (PBE-CPCM/6-31G*)

***L*$_{ZE}$**

N	-0.744012	-0.738747	0.179882
C	-0.069795	0.415422	0.220569
C	1.433294	0.427695	0.092078
N	2.302810	-0.296021	0.844816
C	3.601968	0.010299	0.475102
C	3.524846	0.949516	-0.519148
N	2.181174	1.202134	-0.736453
H	4.457850	-0.451440	0.960458
N	-0.498841	1.654506	0.474599
C	1.943893	-1.241481	1.904257
H	2.694477	-1.167806	2.703666
H	1.919910	-2.264902	1.500203
H	0.951206	-0.982006	2.294371
C	-1.834553	1.999207	0.674366
C	-4.471212	3.007522	1.121378
C	-2.088794	3.393013	0.822241
C	-2.954613	1.121664	0.765820
C	-4.243462	1.628956	0.985446
C	-3.377023	3.888239	1.037472
H	-2.785185	0.048449	0.662031
H	-5.085955	0.929705	1.050511
H	-3.531008	4.968293	1.143946
H	-5.482930	3.391264	1.291024
C	-0.230398	-1.891700	-0.401196
C	0.640731	-4.355868	-1.558467
C	-0.595497	-3.148239	0.160333
C	0.562630	-1.916760	-1.584578
C	0.990704	-3.128416	-2.143901
C	-0.163668	-4.352321	-0.404251
H	1.592947	-3.111342	-3.059991
H	-0.460152	-5.300229	0.059653
H	0.973219	-5.299489	-2.003093
H	-1.231876	4.074081	0.764060
H	0.801995	-0.974780	-2.090280
H	-1.224866	-3.146988	1.057582
H	4.300459	1.461737	-1.082784
C	1.646207	2.130950	-1.735985
H	2.452505	2.812842	-2.037752
H	0.815582	2.683125	-1.275289
H	1.285434	1.569917	-2.612696

***TS*$_{ZE-EE}$**

N	-0.799744	-0.812277	0.046159
C	-0.112676	0.294055	0.228583
C	1.404001	0.331930	0.110596
N	2.294156	-0.304308	0.920808
C	3.579884	0.110991	0.610753
C	3.475177	1.017475	-0.410431
N	2.128251	1.152571	-0.698159
H	4.445932	-0.264664	1.149557
N	-0.635628	1.510257	0.451063
C	1.961659	-1.258847	1.982677
H	2.902710	-1.615787	2.421308
H	1.402980	-2.108198	1.561096
H	1.360938	-0.762142	2.758878
C	-0.920249	2.119754	1.637073
C	-1.563276	3.492602	4.078048
C	-1.285569	3.502028	1.649974
C	-0.905079	1.451667	2.902852
C	-1.214577	2.130207	4.086660
C	-1.598232	4.163065	2.840496
H	-0.671574	0.380917	2.931290
H	-1.186801	1.579410	5.035358
H	-1.871188	5.224886	2.802366
H	-1.804570	4.016355	5.008429
C	-0.234829	-1.969640	-0.505734
C	0.731743	-4.402824	-1.612176
C	-0.533367	-3.218264	0.098858
C	0.534805	-1.974247	-1.697930
C	1.009599	-3.177416	-2.238194
C	-0.046909	-4.414016	-0.442181
H	1.594097	-3.155734	-3.164933
H	-0.284633	-5.363632	0.049909
H	1.102621	-5.339793	-2.040024
H	-1.314301	4.037188	0.693573
H	0.718507	-1.030092	-2.221622
H	-1.151519	-3.223185	1.003245
H	4.233261	1.576347	-0.953179
C	1.572625	1.997350	-1.758168
H	2.253022	2.844559	-1.920647
H	0.588517	2.353820	-1.421573
H	1.473249	1.416319	-2.688942

***L*$_{EE}$**

N	-1.799814	-1.184109	0.086438
C	-1.147000	-0.021467	0.180858
C	0.346034	0.006108	-0.062376
N	1.284787	-0.757001	0.556037
C	2.537732	-0.442351	0.060098
C	2.361850	0.535354	-0.883770
N	1.004869	0.799601	-0.946976
H	3.436412	-0.933608	0.424416
N	-1.779629	1.117344	0.479556
C	1.030596	-1.756984	1.595745
H	1.818170	-1.677165	2.358545
H	1.033008	-2.763250	1.150524
H	0.047501	-1.563784	2.044547
C	-1.130589	2.212485	1.034124
C	0.025652	4.564196	2.180488
C	-1.561068	3.516129	0.653851
C	-0.121818	2.132955	2.037614
C	0.445174	3.288931	2.591282
C	-0.989273	4.664373	1.211259
H	0.181925	1.149919	2.414009
H	1.214980	3.188444	3.365527
H	-1.341275	5.650754	0.887456
H	0.467267	5.464631	2.619565
C	-1.309091	-2.261694	-0.640815
C	-0.464599	-4.575910	-2.089737
C	-1.510269	-3.574536	-0.128494

C	-0.699528	-2.153255	-1.923661
C	-0.283269	-3.291720	-2.627305
C	-1.089140	-4.705230	-0.835642
H	0.176144	-3.172218	-3.615714
H	-1.252366	-5.700038	-0.405186
H	-0.141620	-5.462454	-2.645132
H	-2.356016	3.596682	-0.096168
H	-0.597935	-1.164722	-2.384836
H	-2.001263	-3.676807	0.845936
H	3.075538	1.058730	-1.515018
C	0.386084	1.791070	-1.829856
H	0.246829	2.738361	-1.286282
H	-0.591660	1.420192	-2.166470
H	1.046672	1.942045	-2.694439

$TS1_{ZE}$

N	-0.853640	-0.773459	-1.011742
C	-0.125712	-0.094032	-0.101879
C	1.352241	-0.189484	-0.372119
N	2.182901	0.868058	-0.566151
C	3.465020	0.406758	-0.800269
C	3.414833	-0.962672	-0.759360
N	2.101416	-1.314809	-0.507207
H	4.288843	1.088541	-0.994913
H	4.190972	-1.711916	-0.893978
N	-0.587707	0.604571	0.922035
C	1.790128	2.280919	-0.552483
H	0.797654	2.387768	-1.011482
H	2.530642	2.846315	-1.133597
H	1.757786	2.647927	0.484850
C	1.628410	-2.690540	-0.316755
H	2.190012	-3.345782	-0.996587
H	0.557814	-2.724660	-0.556205
H	1.801231	-2.997705	0.726949
C	0.205428	0.940973	2.019344
C	1.671773	1.708505	4.335498
C	1.099936	0.037995	2.654767
C	0.039853	2.226663	2.601451
C	0.770136	2.604032	3.733489
C	1.822141	0.422999	3.792505
H	1.185622	-0.987271	2.278525
H	-0.670300	2.918969	2.136346
H	0.629463	3.605875	4.154434
H	2.499349	-0.296735	4.266144
H	2.234188	2.003380	5.227167
C	-2.263920	-0.805278	-0.943316
C	-5.089298	-0.986144	-1.030272
C	-2.904158	-2.050780	-1.139525
C	-3.065473	0.353365	-0.803209
C	-4.462522	0.257644	-0.847385
C	-4.302108	-2.139396	-1.175394
H	-2.285234	-2.946076	-1.257803
H	-2.583355	1.322912	-0.654341
H	-5.067124	1.164847	-0.738164
H	-4.777750	-3.115533	-1.320905
H	-6.181665	-1.055033	-1.061195
H	0.675243	-0.093289	-2.757819
C	-0.293149	-0.399433	-3.133301
H	-1.198089	0.196838	-3.094164
Cl	0.262205	0.802171	-5.074830
Cl	-0.434038	-2.017998	-3.727153

$TS1_{EE}$

N	1.230021	0.501587	-1.016066
C	0.004238	0.453619	-0.461558
C	1.332745	1.918112	-2.685718
C	-0.193332	-0.467348	0.712591
N	0.540080	-0.490446	1.856543
C	0.045742	-1.472651	2.694995
C	-1.009467	-2.062656	2.048695
N	-1.142805	-1.431821	0.826080
H	0.483868	-1.661877	3.671629
H	-1.667017	-2.875068	2.347470
N	-0.988587	1.207373	-0.912074
Cl	1.328287	3.926227	-3.878153
Cl	1.516407	0.747147	-3.958364
C	1.674673	0.384132	2.170478
H	2.586045	0.002025	1.684849
H	1.802825	0.394533	3.260975
H	1.464280	1.401342	1.811897
C	-2.161669	-1.762390	-0.175117
H	-2.413618	-2.826065	-0.068485
H	-1.759975	-1.572954	-1.179743
H	-3.055553	-1.140471	-0.015103
C	-2.129723	1.504199	-0.166039
C	-4.527950	2.213005	1.194470
C	-2.121395	1.820031	1.218818
C	-3.368318	1.590109	-0.855602
C	-4.546483	1.930043	-0.182841
C	-3.306674	2.162695	1.884382
H	-1.170365	1.838126	1.762003
H	-3.379456	1.376283	-1.929797
H	-5.488294	1.979931	-0.740613
H	-3.268866	2.407460	2.951950
H	-5.449962	2.486175	1.717463
C	2.161094	-0.537381	-0.977436
C	4.156771	-2.560218	-0.990750
C	3.537084	-0.208212	-0.859440
C	1.814505	-1.904608	-1.136655
C	2.801647	-2.898966	-1.128383
C	4.516665	-1.206934	-0.866352
H	3.818892	0.845310	-0.755846
H	0.767767	-2.177793	-1.304173
H	2.507665	-3.947179	-1.252156
H	5.571244	-0.926374	-0.770604
H	4.925507	-3.339452	-0.994971
H	2.243608	2.254184	-2.202981
H	0.317853	2.127217	-2.350267

$\{[\mathit{L}CH_2Cl^+]Cl^-\}$

N	0.642218	-0.788071	0.244235
C	-0.387834	-0.272533	-0.577825
C	1.682209	-1.571545	-0.326002
C	-1.744478	-0.173297	0.026573
N	-2.569040	0.899377	-0.119059
C	-3.766612	0.633120	0.506936
C	-3.681977	-0.631454	1.034313

N	-2.431345	-1.119933	0.724270
H	-4.574957	1.359546	0.522455
H	-4.404814	-1.227538	1.585496
N	-0.326076	0.105256	-1.813574
Cl	1.254585	-3.395732	-0.523295
Cl	0.549919	4.033841	0.447979
C	-2.262758	2.162134	-0.809152
H	-1.331544	2.605182	-0.405945
H	-3.102907	2.844350	-0.623075
H	-2.157073	1.971011	-1.885401
C	-1.975758	-2.467080	1.082783
H	-1.536728	-2.452952	2.091450
H	-1.228939	-2.811329	0.356362
H	-2.847108	-3.135708	1.060613
C	0.859505	0.361896	-2.529225
C	3.116479	0.989169	-4.093146
C	1.788950	1.328856	-2.076523
C	1.053653	-0.264986	-3.779857
C	2.188502	0.036533	-4.543503
C	2.902807	1.639257	-2.866906
H	1.604870	1.859002	-1.134037
H	0.316881	-0.994815	-4.129743
H	2.339941	-0.467523	-5.503795
H	3.609099	2.399840	-2.517070
H	3.994560	1.232697	-4.699741
C	0.644357	-0.543617	1.662219
C	0.683025	-0.032188	4.422785
C	0.322486	0.740621	2.140296
C	1.010322	-1.566037	2.559923
C	1.034655	-1.300766	3.935811
C	0.330415	0.982958	3.520916
H	0.131021	1.567599	1.444189
H	1.263144	-2.563129	2.187489
H	1.321898	-2.097814	4.629061
H	0.088092	1.986930	3.884214
H	0.697742	0.166795	5.498994
H	2.568191	-1.558114	0.318287
H	1.924430	-1.262521	-1.346838

LCH_2Cl^+

N	0.510316	-0.606192	0.617044
C	-0.514257	-0.328905	-0.316894
C	1.175491	-1.866367	0.605622
C	-1.633015	0.531157	0.153341
N	-2.177742	1.544285	-0.575236
C	-3.231278	2.087988	0.127077
C	-3.342770	1.389005	1.302986
N	-2.353705	0.429071	1.303511
H	-3.809635	2.919444	-0.267248
H	-4.045970	1.484009	2.126665
N	-0.637458	-0.740216	-1.538239
Cl	0.292820	-3.210910	1.568514
C	-1.748750	2.011070	-1.901967
H	-0.656322	2.130259	-1.921200
H	-2.229729	2.981649	-2.080576
H	-2.054636	1.283620	-2.666183
C	-2.175641	-0.549252	2.382591
H	-3.171477	-0.852124	2.734412
H	-1.609511	-0.090407	3.206932
H	-1.637665	-1.425616	2.001160
C	0.377712	-1.334567	-2.310342
C	2.288697	-2.460859	-4.051508
C	1.646994	-0.726297	-2.466673
C	0.069513	-2.497091	-3.051184
C	1.029474	-3.063258	-3.898931
C	2.586297	-1.287038	-3.340237
H	1.878528	0.194779	-1.921118
H	-0.920540	-2.949873	-2.939684
H	0.784862	-3.974430	-4.454511
H	3.559795	-0.801078	-3.463834
H	3.030338	-2.898360	-4.726979
C	0.906374	0.387848	1.576505
C	1.722652	2.344877	3.421507
C	1.036299	1.730085	1.169208
C	1.203539	0.022034	2.903875
C	1.618434	1.002101	3.815496
C	1.429389	2.703529	2.097084
H	0.867382	2.006420	0.123309
H	1.102204	-1.019014	3.224670
H	1.850055	0.709960	4.844585
H	1.530435	3.743526	1.771233
H	2.041062	3.106233	4.140040
H	2.160003	-1.776204	1.077760
H	1.251435	-2.284889	-0.402583

{[c-TS2]$^+$Cl$^-$}

N	-0.517972	0.981656	1.331591
C	-0.127056	-0.001607	0.462172
C	-0.268906	0.243491	2.572766
C	-0.245394	0.077755	-0.992651
N	0.702522	-0.299591	-1.892170
C	0.215471	-0.103171	-3.162214
C	-1.053389	0.415712	-3.037253
N	-1.327186	0.519386	-1.692341
N	0.324777	-0.971938	1.237764
Cl	-1.237925	1.765545	4.198634
C	2.026281	-0.863676	-1.603905
H	2.237286	-0.777703	-0.531349
H	2.773999	-0.299122	-2.178746
H	2.018933	-1.917060	-1.931653
C	-2.595469	1.003627	-1.132025
H	-3.366014	0.896439	-1.906340
H	-2.495022	2.060672	-0.843621
H	-2.865934	0.398504	-0.256086
C	0.430771	-2.352929	1.017645
C	0.772359	-5.120409	0.675562
C	-0.333362	-3.043849	0.049404
C	1.344588	-3.059846	1.830217
C	1.511269	-4.437174	1.655408
C	-0.146647	-4.419948	-0.122817
H	-1.075016	-2.514285	-0.556983
H	1.922506	-2.512556	2.581282
H	2.225008	-4.978247	2.284436
H	-0.730588	-4.947570	-0.883213
H	0.907731	-6.197397	0.537079
C	-0.292787	2.384554	1.083872
C	0.121317	5.082250	0.480595
C	0.940201	2.795884	0.546558

C	-1.322822	3.311223	1.318761
C	-1.106996	4.662035	1.016962
C	1.142496	4.149845	0.244382
H	1.736223	2.061954	0.380737
H	-2.271218	2.967209	1.736882
H	-1.904883	5.388757	1.198471
H	2.101839	4.473696	-0.170954
H	0.281708	6.139324	0.245924
H	0.650102	0.430076	3.126662
H	-1.042101	-0.419090	2.953485
H	0.792601	-0.394138	-4.035825
Cl	0.931424	-3.278749	-4.047623
H	-1.784723	0.700463	-3.789481

c-TS2^{+}

N	0.881881	0.522419	1.221785
C	-0.083717	0.091057	0.358200
C	0.127938	0.292269	2.458093
C	-0.002490	0.153822	-1.101047
N	-0.337198	-0.853410	-1.952472
C	-0.131318	-0.426586	-3.243574
C	0.338846	0.865381	-3.179774
N	0.413734	1.210775	-1.850130
H	-0.328172	-1.071654	-4.096251
H	0.618945	1.562550	-3.965761
N	-1.049140	-0.363934	1.139831
Cl	1.619426	1.362890	4.075179
C	-0.828124	-2.183773	-1.568849
H	-0.197412	-2.589969	-0.765183
H	-0.766503	-2.830981	-2.452723
H	-1.871851	-2.107908	-1.229155
C	0.856595	2.517518	-1.343309
H	0.786195	3.238294	-2.167872
H	1.897135	2.443272	-0.993680
H	0.202646	2.832215	-0.518605
C	-2.430976	-0.449448	0.911235
C	-5.203118	-0.712467	0.554172
C	-3.113603	0.419881	0.029087
C	-3.146666	-1.429179	1.634237
C	-4.526828	-1.557921	1.449334
C	-4.493956	0.274382	-0.150421
H	-2.571232	1.219594	-0.485471
H	-2.605255	-2.084224	2.323417
H	-5.076889	-2.322418	2.006635
H	-5.020960	0.949329	-0.832115
H	-6.283637	-0.814003	0.414207
C	2.293386	0.332126	0.995830
C	5.008881	-0.024257	0.442966
C	2.748155	-0.910377	0.518520
C	3.184586	1.399621	1.197763
C	4.544804	1.212834	0.919702
C	4.111398	-1.083658	0.241710
H	2.042262	-1.737505	0.384450
H	2.807745	2.352557	1.575361
H	5.244656	2.039508	1.075835
H	4.469907	-2.050194	-0.125634
H	6.073360	-0.162419	0.228947
H	0.340157	-0.596101	3.051654
H	-0.543593	1.070091	2.813875

{[c-*L*CH$_2^{2+}$]Cl^{-}}

N	-0.929081	0.959785	0.543430
C	-0.112991	-0.043008	0.119352
C	-1.366973	0.098993	1.668497
C	0.827123	-0.171602	-0.973284
N	2.099538	-0.651046	-0.854520
C	2.670721	-0.683112	-2.100129
C	1.737282	-0.206207	-2.996960
N	0.600684	0.086538	-2.291940
N	-0.439672	-0.914999	1.114341
Cl	2.195517	3.011397	-3.113389
C	2.770732	-1.050598	0.389892
H	2.512499	-0.344087	1.190642
H	3.852831	-1.020892	0.209779
H	2.465630	-2.071817	0.664491
C	-0.598709	0.685943	-2.887029
H	-0.351357	1.729086	-3.147075
H	-1.431028	0.641756	-2.173491
H	-0.855728	0.117012	-3.791130
C	-0.379568	-2.307306	1.331685
C	-0.258875	-5.048332	1.864647
C	-0.074238	-3.202029	0.286856
C	-0.633769	-2.772804	2.636418
C	-0.579757	-4.147019	2.892214
C	-0.005481	-4.571736	0.568610
H	0.075662	-2.843398	-0.735465
H	-0.857856	-2.063793	3.439423
H	-0.778994	-4.511864	3.904150
H	0.228911	-5.270802	-0.239689
H	-0.211419	-6.121485	2.071829
C	-1.069116	2.352600	0.377231
C	-1.448282	5.110115	0.116872
C	-0.204556	3.090913	-0.451963
C	-2.123396	2.979306	1.072989
C	-2.300119	4.360317	0.944167
C	-0.410555	4.469545	-0.577628
H	0.628986	2.636463	-1.001072
H	-2.800921	2.392955	1.701767
H	-3.113681	4.848547	1.488851
H	0.262430	5.037034	-1.227451
H	-1.593827	6.189607	0.014456
H	-2.419119	-0.217877	1.619246
H	-1.073664	0.501213	2.649478
H	3.697144	-1.009940	-2.248604
H	1.797039	-0.053375	-4.070496

{[c-*L*CH$_2^{2+}$][Cl^{-}]$_2$}

N	-0.622738	-0.463946	1.196993
C	-0.042099	0.056093	0.087856
C	-1.683591	0.566268	1.088862
C	1.120459	-0.353164	-0.674850
N	2.330976	-0.724062	-0.171657
C	3.154562	-1.051162	-1.220431
C	2.435755	-0.879299	-2.383527
N	1.179861	-0.450139	-2.033291
N	-0.942079	1.048204	-0.098972

Cl	-2.705847	-1.686777	-1.388386
C	2.715423	-0.740080	1.246305
H	2.358956	0.195930	1.721255
H	2.272655	-1.622782	1.733283
H	3.810374	-0.801479	1.290470
C	0.079427	-0.184063	-2.970119
H	0.348229	-0.637636	-3.932947
H	-0.039745	0.903893	-3.091051
H	-0.850334	-0.640390	-2.573926
C	-0.985777	2.280010	-0.775394
C	-1.162576	4.706015	-2.151784
C	0.190614	2.892590	-1.249907
C	-2.246369	2.874516	-0.974657
C	-2.325219	4.094250	-1.655809
C	0.088429	4.101627	-1.948517
H	1.167928	2.455208	-1.030430
H	-3.149983	2.375765	-0.610905
H	-3.303077	4.560375	-1.809679
H	0.999341	4.584456	-2.315524
H	-1.229605	5.655898	-2.690808
C	-0.621087	-1.715624	1.843834
C	-0.600807	-4.156534	3.204257
C	-1.074036	-1.770202	3.175708
C	-0.172519	-2.874296	1.180510
C	-0.152132	-4.089499	1.875747
C	-1.070136	-2.998747	3.845676
H	-1.409571	-0.857510	3.677703
H	0.104537	-2.831239	0.123829
H	0.192196	-4.993076	1.363566
H	-1.423854	-3.047090	4.880014
H	-0.593285	-5.112281	3.737138
H	-2.654222	0.112615	0.834123
H	-1.689164	1.300525	1.907533
H	4.180762	-1.371283	-1.057913
Cl	1.305740	2.323752	2.218671
H	2.713629	-1.035630	-3.422849

c-$L\mathrm{CH_2}^{2+}$

N	0.306310	-0.955974	1.026362
C	0.001140	0.000643	0.111482
C	-0.010049	0.012783	2.107000
H	-0.881793	-0.290694	2.705111
H	0.854780	0.323403	2.711431
C	0.009159	-0.008226	-1.336866
N	1.014702	-0.474683	-2.128497
C	0.647200	-0.309929	-3.440336
C	-0.604617	0.269729	-3.450764
N	-0.987221	0.449257	-2.145214
H	1.300152	-0.609192	-4.257110
H	-1.247735	0.559786	-4.278557
N	-0.313884	0.968275	1.011258
C	-2.260043	1.039203	-1.706187
H	-2.963644	0.983949	-2.546354
H	-2.097594	2.090120	-1.421735
H	-2.654851	0.468224	-0.854551
C	2.282787	-1.059029	-1.668578
H	2.998673	-1.004488	-2.498350
H	2.119809	-2.109484	-1.382607
H	2.663109	-0.483389	-0.813545
C	0.376692	-2.366435	1.053008
C	0.574782	-5.148457	1.179580
C	1.011532	-2.965672	2.157704
C	-0.169059	-3.144475	0.013482
C	-0.053711	-4.537979	0.082269
C	1.097806	-4.360516	2.217450
H	1.440573	-2.344923	2.950323
H	-0.706333	-2.676653	-0.816881
H	-0.479295	-5.149061	-0.719158
H	1.586401	-4.831217	3.075512
H	0.650435	-6.238673	1.228488
C	-0.387400	2.378720	1.020323
C	-0.594761	5.161323	1.111070
C	-1.033299	2.989465	2.112290
C	0.165107	3.145559	-0.023973
C	0.044971	4.539444	0.026719
C	-1.124260	4.384643	2.154134
H	-1.467314	2.377031	2.908636
H	0.711044	2.669339	-0.843847
H	0.475512	5.142017	-0.778475
H	-1.621632	4.864424	3.002059
H	-0.674182	6.251818	1.145894

{[$\mathrm{TS2_{EE}}^{+}$]Cl^{-}}

N	1.250066	-0.390879	1.233976
C	0.361312	-0.279901	2.335508
C	1.401608	0.684144	0.414357
C	0.537426	-1.272867	3.429984
N	-0.424031	-2.116229	3.883426
C	0.083865	-2.842514	4.940616
C	1.374746	-2.420923	5.144312
N	1.640810	-1.448171	4.202541
N	-0.511648	0.671055	2.338602
C	0.166246	0.975898	-2.407621
C	-0.812983	1.056656	-3.552370
N	-1.385775	2.186744	-4.042525
C	-2.236551	1.854816	-5.081508
C	-2.182393	0.493250	-5.229112
N	-1.300659	0.016341	-4.276212
H	-2.805004	2.610892	-5.617188
H	-2.684783	-0.172515	-5.926197
N	1.296916	1.670338	-2.437126
N	-0.142898	0.170471	-1.376499
Cl	3.066060	2.099253	1.562089
C	-1.146670	3.549350	-3.558216
H	-0.185545	3.919607	-3.946079
H	-1.121156	3.553040	-2.459385
H	-1.969567	4.184906	-3.911045
C	-0.945466	-1.396216	-4.108177
H	-0.053348	-1.466214	-3.473044
H	-0.742173	-1.827032	-5.099023
H	-1.778819	-1.928857	-3.626194
C	-1.763694	-2.316572	3.315137
H	-1.815394	-3.340464	2.893822
H	-1.932329	-1.584854	2.515658
H	-2.506845	-2.174811	4.113316
C	2.912758	-0.724144	4.086603
H	2.781737	0.174682	3.463283
H	3.664062	-1.384191	3.627758

H	3.234721	-0.429643	5.095419
C	2.033894	-1.583141	0.994526
C	3.568865	-3.865863	0.458188
C	1.423639	-2.849408	0.997882
C	3.405444	-1.449486	0.713834
C	4.164990	-2.594764	0.438762
C	2.200716	-3.987570	0.740842
H	0.350121	-2.969049	1.169770
H	3.864625	-0.456024	0.728395
H	5.232026	-2.488845	0.218885
H	1.711503	-4.967058	0.749867
H	4.168121	-4.757466	0.248549
C	-1.282155	1.033267	3.456000
C	-2.910459	1.895744	5.590004
C	-2.654351	1.301581	3.244002
C	-0.725885	1.235525	4.741385
C	-1.540417	1.669626	5.795093
C	-3.461908	1.708852	4.311294
H	-3.068877	1.166752	2.239860
H	0.348935	1.100944	4.896524
H	-1.096831	1.837483	6.782035
H	-4.527184	1.895126	4.140369
H	-3.542433	2.232144	6.418061
C	1.847692	2.200751	-3.601628
C	3.129487	3.374685	-5.860359
C	2.490330	3.466041	-3.511449
C	1.895806	1.527052	-4.852375
C	2.525384	2.111421	-5.960405
C	3.110550	4.043821	-4.623713
H	2.484006	3.979522	-2.543664
H	1.475637	0.519080	-4.938974
H	2.553704	1.563870	-6.909488
H	3.589993	5.024120	-4.522897
H	3.623328	3.824344	-6.727736
C	-1.453440	-0.197185	-1.061621
C	-4.057364	-1.033248	-0.270783
C	-2.540489	0.717890	-1.032102
C	-1.707797	-1.537429	-0.670328
C	-2.989192	-1.947095	-0.282443
C	-3.821955	0.299437	-0.649236
H	-2.362371	1.771737	-1.271053
H	-0.883556	-2.256830	-0.701084
H	-3.148774	-2.990054	0.014392
H	-4.641957	1.026502	-0.635731
H	-5.058364	-1.353823	0.035167
H	0.731578	1.523939	0.552973
H	2.054331	0.615756	-0.448244
Cl	-1.439518	-5.420586	1.601839
H	2.118547	-2.721367	5.878044
H	-0.512577	-3.595165	5.449885

$TS2_{EE}^{+}$

N	1.020924	-0.045134	1.311312
C	0.198068	-0.233742	2.446047
C	0.868092	1.068502	0.543865
C	0.678314	-1.234100	3.439020
N	-0.015536	-2.333300	3.832401
C	0.701730	-2.987232	4.813701
C	1.850967	-2.267683	5.025374
N	1.821776	-1.185316	4.169260
H	0.336534	-3.902941	5.271988
H	2.678185	-2.428705	5.712380
N	-0.888273	0.454439	2.561583
C	0.084864	0.764311	-2.348631
C	-0.813576	0.929474	-3.547829
N	-1.078812	2.096848	-4.187787
C	-1.954785	1.856934	-5.231461
C	-2.231926	0.514608	-5.225936
N	-1.521557	-0.042394	-4.177783
H	-2.304181	2.657991	-5.877910
H	-2.862951	-0.089031	-5.873363
N	1.357198	1.135975	-2.408804
N	-0.441011	0.241602	-1.223876
Cl	2.236577	2.775139	1.750453
C	-0.515396	3.408142	-3.851259
H	0.474450	3.518920	-4.320007
H	-0.415207	3.495772	-2.760700
H	-1.201156	4.180324	-4.224314
C	-1.524542	-1.467313	-3.834795
H	-0.677646	-1.675156	-3.168323
H	-1.429003	-2.050988	-4.761417
H	-2.464227	-1.720628	-3.321458
C	-1.319142	-2.772990	3.321200
H	-1.282589	-3.860663	3.168971
H	-1.524077	-2.270273	2.367058
H	-2.102076	-2.517316	4.050479
C	2.861713	-0.150588	4.097039
H	2.482347	0.726270	3.549655
H	3.740265	-0.558088	3.575553
H	3.130669	0.139589	5.122604
C	2.019558	-1.019775	0.934607
C	3.943158	-2.885362	0.131645
C	1.639145	-2.352602	0.704590
C	3.348505	-0.605853	0.745580
C	4.306090	-1.545309	0.339653
C	2.610685	-3.285073	0.314793
H	0.590785	-2.652923	0.796887
H	3.614674	0.441159	0.924709
H	5.342360	-1.225319	0.192242
H	2.315982	-4.323643	0.134788
H	4.695993	-3.615290	-0.181672
C	-1.668178	0.503644	3.728976
C	-3.354947	0.686016	5.982523
C	-3.071726	0.410086	3.580650
C	-1.120836	0.728898	5.014402
C	-1.965779	0.823400	6.127638
C	-3.901924	0.479561	4.704773
H	-3.488927	0.264175	2.578879
H	-0.042864	0.879047	5.129513
H	-1.531812	1.012810	7.114991
H	-4.985576	0.385829	4.579450
H	-4.009222	0.757340	6.857025
C	2.051060	1.325702	-3.603117
C	3.637075	1.745360	-5.930060
C	2.982834	2.395489	-3.674501
C	1.959074	0.454366	-4.721252
C	2.740224	0.667727	-5.865186
C	3.754717	2.603646	-4.822426
H	3.082218	3.056178	-2.806154

H	1.307325	-0.424275	-4.668432
H	2.654981	-0.026688	-6.708742
H	4.460172	3.441593	-4.850390
H	4.248652	1.905610	-6.823639
C	-1.820649	0.229530	-0.971367
C	-4.576932	0.126558	-0.286889
C	-2.636863	1.386223	-1.056122
C	-2.416447	-0.974872	-0.517183
C	-3.776002	-1.025063	-0.185158
C	-3.996420	1.329476	-0.720269
H	-2.187435	2.340668	-1.350886
H	-1.787998	-1.869231	-0.438829
H	-4.214574	-1.970747	0.152330
H	-4.605289	2.237818	-0.788835
H	-5.639474	0.087292	-0.026414
H	0.031424	1.722147	0.771635
H	1.508182	1.203419	-0.329047

{[$TS2_{ZE}^{+}$]Cl^{-}}

N	0.863463	0.496496	-1.252595
C	-0.355843	0.765800	-1.951819
C	0.941719	-0.618136	-0.498571
C	-0.251693	1.677217	-3.121995
N	-0.955178	2.826995	-3.284281
C	-0.644923	3.369071	-4.513541
C	0.252306	2.524370	-5.119167
N	0.485371	1.481466	-4.247259
H	-1.084036	4.306086	-4.846432
H	0.733490	2.570184	-6.092979
N	-1.434280	0.197955	-1.535236
C	0.211193	-1.257663	2.474140
C	1.472794	-2.055866	2.257252
N	2.744997	-1.662670	2.532090
C	3.623722	-2.671990	2.179385
C	2.874519	-3.695090	1.659867
N	1.550478	-3.298096	1.713799
H	4.696167	-2.571758	2.326304
H	3.164900	-4.654638	1.239982
N	-0.784240	-1.752983	3.199193
N	0.270078	-0.079807	1.823981
Cl	1.661052	-2.531120	-2.120193
C	3.129767	-0.403418	3.177993
H	2.415170	0.370845	2.869495
H	4.143916	-0.141917	2.846578
C	0.436240	-4.071211	1.153956
H	-0.500737	-3.537679	1.355951
H	0.409939	-5.061720	1.630703
H	0.589613	-4.165014	0.067179
C	-1.845513	3.470370	-2.309078
H	-1.394127	4.439410	-2.016955
H	-1.941480	2.829628	-1.424344
H	-2.830746	3.613352	-2.776480
C	1.367884	0.343272	-4.532556
H	1.174087	-0.476843	-3.823996
H	2.415524	0.667426	-4.443688
H	1.165216	0.000018	-5.556979
C	2.032229	1.340034	-1.413179
C	4.323412	2.928622	-1.665060
C	1.925857	2.735697	-1.287610
C	3.275822	0.731098	-1.660501
C	4.418908	1.532868	-1.778855
C	3.076754	3.524264	-1.423942
H	0.972014	3.224468	-1.066487
H	3.334264	-0.356116	-1.778329
H	5.386544	1.059243	-1.972620
H	2.976922	4.609953	-1.326409
H	5.219138	3.549945	-1.763090
C	-2.654083	0.189568	-2.230677
C	-5.180866	0.076776	-3.470434
C	-3.831122	0.378247	-1.469636
C	-2.755810	-0.092731	-3.613370
C	-4.016471	-0.153697	-4.220003
C	-5.082017	0.343918	-2.094656
H	-3.738701	0.572402	-0.396116
H	-1.855761	-0.317270	-4.193753
H	-4.087736	-0.390404	-5.286623
H	-5.986124	0.511517	-1.500570
H	-6.162303	0.030294	-3.952824
C	-0.615257	-2.813208	4.091285
C	-0.453830	-4.972553	5.940323
C	0.471176	-2.922030	5.000861
C	-1.636385	-3.797569	4.163133
C	-1.548123	-4.863745	5.064075
C	0.547255	-3.989345	5.906167
H	1.236774	-2.138480	5.023490
H	-2.493259	-3.709019	3.486163
H	-2.345159	-5.615436	5.087135
H	1.394485	-4.043964	6.599320
H	-0.392007	-5.803437	6.650468
C	-0.727578	0.901904	1.894375
C	-2.570382	3.074169	1.897051
C	-2.084836	0.706822	2.271816
C	-0.328784	2.212156	1.520667
C	-1.230751	3.281795	1.524327
C	-2.982966	1.784016	2.268632
H	-2.412780	-0.288619	2.573590
H	0.716593	2.371106	1.236014
H	-0.887703	4.279408	1.226702
H	-4.023150	1.609356	2.568031
H	-3.280767	3.907444	1.900295
H	0.064387	-1.248963	-0.425415
H	1.871884	-0.814240	0.018045
Cl	0.234535	6.146449	-1.234110
H	3.114950	-0.525057	4.272599

$TS2_{ZE}^{+}$

N	1.648723	0.519884	0.245177
C	0.975454	1.750488	0.523691
C	1.166194	-0.259302	-0.745314
C	1.760734	2.793647	1.229977
N	1.395781	3.372335	2.404361
C	2.311238	4.354630	2.720012
C	3.249152	4.376509	1.717369
N	2.895020	3.406559	0.803002
H	2.220058	4.946837	3.627112
H	4.128513	5.000028	1.575491
N	-0.249880	1.873544	0.142033
C	-1.300492	-2.173871	-0.772341

C	-0.472904	-2.703589	-1.918171
N	0.426404	-3.721634	-1.869207
C	0.982646	-3.903984	-3.122897
C	0.426465	-2.964240	-3.950973
N	-0.467835	-2.231561	-3.191724
H	1.720496	-4.679652	-3.312233
H	0.600207	-2.741351	-5.000540
N	-2.622439	-2.122490	-0.860455
N	-0.511874	-1.779628	0.247074
Cl	2.287110	0.634124	-2.927418
C	0.706593	-4.558520	-0.697956
H	-0.032234	-5.372942	-0.634748
H	0.652838	-3.924869	0.197176
H	1.714657	-4.979596	-0.811126
C	-1.197412	-1.061335	-3.692804
H	-1.867930	-0.691425	-2.907081
H	-1.786750	-1.354887	-4.573497
H	-0.466244	-0.282827	-3.961904
C	0.209330	3.045027	3.204758
H	0.420588	3.310499	4.248959
H	-0.004340	1.968753	3.134786
H	-0.652353	3.621458	2.834454
C	3.623998	3.128024	-0.441120
H	2.999558	2.525310	-1.119063
H	4.549425	2.582433	-0.204302
H	3.865202	4.088018	-0.919393
C	2.882038	0.159339	0.916045
C	5.273529	-0.573974	2.171134
C	2.977081	0.221033	2.317574
C	3.969946	-0.273839	0.138103
C	5.161858	-0.645770	0.774485
C	4.181724	-0.138371	2.937367
H	2.112856	0.506447	2.922639
H	3.877999	-0.290508	-0.953098
H	6.009536	-0.982619	0.169697
H	4.255486	-0.094265	4.028263
H	6.208089	-0.860767	2.663117
C	-0.980220	3.070130	0.149287
C	-2.617026	5.365086	0.129109
C	-2.349302	2.976588	0.497081
C	-0.450308	4.320165	-0.252999
C	-1.272009	5.453655	-0.264572
C	-3.151415	4.122017	0.507893
H	-2.753069	1.999067	0.778653
H	0.581346	4.391255	-0.610437
H	-0.858331	6.412171	-0.594237
H	-4.203787	4.040702	0.798259
H	-3.251285	6.256957	0.119905
C	-3.341574	-2.867354	-1.798830
C	-4.949779	-4.309321	-3.649386
C	-3.101936	-4.242182	-2.062188
C	-4.433641	-2.246587	-2.459608
C	-5.214707	-2.955378	-3.378474
C	-3.895119	-4.947016	-2.977684
H	-2.315335	-4.765206	-1.507395
H	-4.643701	-1.193578	-2.242446
H	-6.042922	-2.447452	-3.885106
H	-3.691672	-6.008651	-3.157539
H	-5.568825	-4.863221	-4.362389
C	-0.999416	-1.340397	1.484224
C	-1.723158	-0.478876	4.104864
C	-2.300232	-0.830917	1.754800
C	-0.080549	-1.401426	2.565622
C	-0.434883	-0.982335	3.852946
C	-2.644074	-0.409046	3.046913
H	-3.030555	-0.788693	0.945453
H	0.921259	-1.797464	2.369155
H	0.296217	-1.058153	4.665934
H	-3.654599	-0.025209	3.229173
H	-2.006060	-0.153431	5.111292
H	0.281246	0.085247	-1.263925
H	1.665583	-1.198260	-0.949841

$\{[L_2CH_2^{2+}][Cl^-]_2\}$

N	0.144697	-0.138316	-0.904995
C	0.881556	-0.532433	-2.015697
C	0.851272	0.629965	0.133949
H	0.564961	1.690502	0.052593
C	0.098303	-1.246538	-3.074182
N	-0.311290	-2.537305	-3.066632
C	-0.989643	-2.799806	-4.241611
C	-0.979330	-1.644330	-4.981905
N	-0.298817	-0.692190	-4.245854
H	-1.433719	-3.773850	-4.430963
N	2.142369	-0.255526	-2.134881
H	1.922878	0.551661	-0.099611
C	-0.110915	0.797938	2.448366
C	-0.541974	2.195919	2.120600
N	-1.837567	2.589435	2.025289
C	-1.881066	3.954989	1.833430
C	-0.584627	4.404147	1.810047
N	0.230728	3.305526	1.993035
H	-2.823343	4.484617	1.719334
N	-0.402599	0.221977	3.575731
N	0.606525	0.119325	1.479341
C	-0.049840	-3.539359	-2.026779
H	-1.007005	-4.045510	-1.795909
H	0.354996	-3.043992	-1.134519
H	0.681908	-4.266880	-2.410991
C	-0.015789	0.676187	-4.694537
H	-0.878040	1.035986	-5.272288
H	0.887213	0.672310	-5.324223
H	0.145898	1.330735	-3.826133
C	1.697243	3.352550	1.969124
H	2.101182	2.434068	2.415203
H	2.025783	4.222136	2.555167
H	2.023392	3.453683	0.919972
C	-3.011972	1.714547	2.122542
H	-3.188033	1.450608	3.176140
H	-2.847541	0.806693	1.525249
H	-3.873790	2.263686	1.722640
C	-1.292510	0.038608	-1.017429
C	-4.062866	0.391861	-1.289653
C	-2.164284	-1.030591	-0.752398
C	-1.803075	1.294112	-1.402388
C	-3.188595	1.463705	-1.534132
C	-3.549141	-0.853871	-0.900636
H	-1.769662	-2.001386	-0.442429
H	-1.108250	2.124013	-1.596494

H	-3.584338	2.437789	-1.840479
H	-4.216748	-1.702271	-0.720087
H	-5.143039	0.527717	-1.404681
C	2.930332	-0.736395	-3.198898
C	4.625695	-1.579390	-5.295249
C	3.132636	-2.112582	-3.445717
C	3.612743	0.212904	-3.994400
C	4.440404	-0.209711	-5.041270
C	3.976297	-2.524763	-4.487635
H	2.660179	-2.854157	-2.793844
H	3.469475	1.277402	-3.781304
H	4.950671	0.537500	-5.658431
H	4.127119	-3.595252	-4.663461
H	5.281197	-1.905890	-6.108877
C	1.159673	-1.180465	1.787621
C	2.278600	-3.697076	2.294197
C	2.549668	-1.306582	1.939912
C	0.324642	-2.305219	1.890655
C	0.888832	-3.563320	2.145459
C	3.106596	-2.568997	2.191839
H	3.187097	-0.419710	1.863702
H	-0.756469	-2.187274	1.779149
H	0.238738	-4.440404	2.225142
H	4.190254	-2.667816	2.310542
H	2.715980	-4.681306	2.490286
C	-0.953525	0.889171	4.680350
C	-2.082232	2.052933	7.001961
C	-0.404178	2.070730	5.234379
C	-2.054675	0.282148	5.332052
C	-2.619703	0.868941	6.469954
C	-0.968455	2.641097	6.384104
H	0.491049	2.516976	4.788655
H	-2.457656	-0.649870	4.922172
H	-3.479891	0.390990	6.950765
H	-0.524462	3.550673	6.803049
H	-2.518030	2.503430	7.899337
H	-1.400559	-1.413706	-5.957027
Cl	-3.362218	-4.811529	-1.888178
H	-0.173657	5.400641	1.670457
Cl	1.006338	3.683042	-1.756688

$\{[L_2CH_2^{2+}][Cl^-]\}^+$

N	-0.666076	-0.916608	1.304390
C	0.266061	-1.856800	0.904080
C	-0.188502	0.428753	1.706186
H	0.523810	0.310015	2.537376
C	-0.298617	-3.113512	0.325863
N	0.030349	-4.373438	0.714111
C	-0.653979	-5.280382	-0.071094
C	-1.414593	-4.560176	-0.955553
N	-1.185376	-3.223124	-0.697731
H	-2.093331	-4.881059	-1.741861
N	1.538521	-1.608982	1.020557
H	-1.069734	0.997353	2.054582
C	-0.274716	1.834379	-0.306528
C	0.271364	3.106575	-0.873039
N	0.479996	3.353268	-2.193681
C	0.926065	4.650088	-2.345672
C	0.983639	5.207174	-1.093301
N	0.575590	4.243917	-0.193500
H	1.163399	5.059929	-3.324140
N	-1.410862	1.322089	-0.681334
N	0.490942	1.219094	0.672570
C	0.956334	-4.752768	1.787164
H	1.029613	-3.937821	2.518995
H	1.950878	-4.954175	1.361564
H	0.561937	-5.655223	2.273517
C	-1.812182	-2.125191	-1.442466
H	-1.358279	-1.168591	-1.150078
H	-2.887089	-2.102054	-1.207952
H	-1.664562	-2.304355	-2.517446
C	0.485811	4.450893	1.257464
H	0.370695	5.529212	1.431928
H	1.412103	4.093998	1.733499
H	-0.389104	3.915901	1.671272
C	0.286651	2.416199	-3.304948
H	1.147535	2.500124	-3.982910
H	-0.643125	2.666503	-3.836925
H	0.217061	1.393018	-2.914657
C	-1.941837	-1.329156	1.833456
C	-4.428063	-2.119360	2.881274
C	-2.012457	-2.374078	2.776369
C	-3.116236	-0.660868	1.437154
C	-4.350928	-1.055484	1.968164
C	-3.255945	-2.776303	3.283304
H	-1.095024	-2.845679	3.142110
H	-3.048885	0.158609	0.718225
H	-5.259776	-0.529989	1.658138
H	-3.301300	-3.590297	4.013822
H	-5.397046	-2.426625	3.287037
C	2.544138	-2.329579	0.364295
C	4.707005	-3.685376	-0.860011
C	3.745659	-2.566212	1.075757
C	2.460659	-2.748384	-0.986725
C	3.534546	-3.421448	-1.585066
C	4.806497	-3.249643	0.472439
H	3.819706	-2.212975	2.109273
H	1.569238	-2.508951	-1.576290
H	3.455757	-3.731252	-2.632756
H	5.721993	-3.434727	1.044199
H	5.542633	-4.209580	-1.334178
C	1.914940	1.401616	0.709850
C	4.702475	1.798134	0.767407
C	2.676697	1.254001	-0.465934
C	2.557168	1.738033	1.918112
C	3.946090	1.922706	1.943115
C	4.061798	1.467012	-0.435625
H	2.193333	0.932351	-1.393528
H	1.972090	1.871618	2.833377
H	4.434487	2.182160	2.887727
H	4.643054	1.348144	-1.355624
H	5.785697	1.952455	0.790422
C	-2.380139	2.057134	-1.390971
C	-4.457392	3.388699	-2.770216
C	-2.861857	3.305620	-0.930306
C	-2.977649	1.469530	-2.530527
C	-3.995306	2.140120	-3.219229
C	-3.892623	3.959083	-1.619438
H	-2.475952	3.718765	0.008159

H	-2.622807	0.493076	-2.876407
H	-4.437614	1.677822	-4.108151
H	-4.263685	4.918017	-1.242088
H	-5.263408	3.902570	-3.303496
Cl	-2.342477	3.013046	2.947905
H	-0.545592	-6.352487	0.072442
H	1.270150	6.203912	-0.767262

***L*CH$_2^{2+}$**

N	1.618784	-0.837044	0.603286
C	0.506520	-0.523939	-0.304939
C	2.370816	-1.870949	0.333670
C	-0.679797	0.095286	0.313012
N	-1.245673	1.271543	-0.075987
C	-2.363944	1.501548	0.692122
C	-2.489445	0.445254	1.563261
N	-1.444907	-0.416372	1.316671
H	-2.972184	2.393365	0.560487
H	-3.234090	0.234614	2.327283
N	0.727725	-0.798933	-1.542927
C	-0.797000	2.156739	-1.159071
H	0.270731	1.995706	-1.356285
H	-0.960634	3.195115	-0.840999
H	-1.382239	1.941481	-2.066015
C	-1.232972	-1.694750	2.009490
H	-2.194809	-2.012427	2.432321
H	-0.499057	-1.561952	2.818152
H	-0.883757	-2.449937	1.291672
C	-0.197396	-0.769945	-2.582755
C	-1.870402	-0.725614	-4.837369
C	-1.586597	-1.030944	-2.439806
C	0.344836	-0.528018	-3.870964
C	-0.494929	-0.479326	-4.984985
C	-2.406601	-1.018845	-3.568949
H	-2.005933	-1.301306	-1.466120
H	1.421642	-0.359674	-3.962669
H	-0.075649	-0.269537	-5.973308
H	-3.471634	-1.246257	-3.463964
H	-2.525497	-0.711062	-5.713773
C	1.873941	-0.004036	1.764051
C	2.459722	1.566171	3.982084
C	1.933005	1.391372	1.613036
C	2.107184	-0.628741	3.001312
C	2.401451	0.170016	4.112648
C	2.229311	2.172258	2.736213
H	1.805350	1.858748	0.633253
H	2.033627	-1.717000	3.094042
H	2.576403	-0.302976	5.083062
H	2.293383	3.258874	2.630653
H	2.685616	2.185631	4.855031
H	3.267804	-2.042904	0.932921
H	2.087291	-2.531235	-0.488851

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