Supporting Information for

Structural Tuning of Ligand-Based Two-Electron Intervalence Charge Transfer

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Experimental Procedures

Materials. All compounds were handled, reactions were performed, and analytical samples were prepared in inert atmosphere using standard Schlenk, dry-box and vacuum-line techniques. Solvents were purchased from VWR Scientific Products and purified using a Braun solvent purification system or using standard solvent purification techniques.¹ Deuterated solvents were purchased from Cambridge Isotope Laboratories, degassed, dried and distilled by procedures similar to those used for non-isotopically enriched solvents. Technical grade ferrocenium tetrafluoroborate (FcBF₄) was purchased from Aldrich, dissolved in acetonitrile and dried over calcium hydride at room temperature; the solvent was degassed and the solid was precipitated with diethylether, collected by filtration and dried in vacuum. Octamethylporphyrinogen, LH₄, was prepared according to standard procedures.² Other reagents were purchased from Aldrich, Alfa Aesar or Strem Chemicals and used as received. Elemental analyses were conducted at H. Kolbe Mikroanalytisches Laboratorium (Mühlheim a. d. Ruhr, Germany).

Synthesis of Li₂(1,4-dioxane)₅[LMg]. LH₄ (10.0 g, 23.3 mmol) was dissolved in 400 mL of 1,4dioxane and 23.5 mL of a 2.0-M Et₂O solution (46.7 mmol, 2 equiv) of ethylmagnesium chloride was added. The resulting white suspension was refluxed overnight, the mixture was cooled down to room temperature and filtered and butyllithium (23.5 mL of a 2.0-M pentane solution, 46.7 mmol, 2 equiv) was added to the filtrate and the mixture was again refluxed overnight. The mixture was then cooled to room temperature and the product was collected by filtration and dried. Yield: 10.98 g (50%). The solid was then recrystallized from 1,4-dioxane. ¹H NMR (500 MHz, CD₃CN): $\delta = 5.66$ (s, 8H, pyrrole), 3.62 (s, 40H, dioxane), 1.49 (s, 24H, Me). Anal. Calcd for C₄₈H₇₂Li₂MgN₄O₁₀: C, 63.82; H, 8.04; N, 6.21. Found: C, 63.73; H, 7.94; N, 6.15.

Synthesis of $[L^{AA}Mg](BF_4)_2$. Two separate 10-mL MeCN solutions of $LMgLi_2(diox)_5$ (0.48 g, 0.53 mmol) and FcBF₄ (0.60 g, 2.11 mmol, 4 equiv.) were prepared. The former was added dropwise to the latter, and the combined green solution was evaporated and dried in vacuum.

The solid residue was triturated in 200 mL of boiling CH_2Cl_2 and the resulting suspension was filtered. The filtrate was evaporated and dried, then triturated in 200 mL hexanes, filtered and dried again. The off-white (greenish) powder was recrystallized from CH_2Cl_2 (80 mL)/hexanes (30 mL). Yield: 0.09 g (30%). ¹H NMR (500 MHz, CD_3CN): $\delta = 7.88$ (d, 5 Hz, 4H, pyrrole), 6.96 (d, 5 Hz, 4H, pyrrole), 2.01 (s, 6H, Me), 1.86 (s, 6H, Me), 1.84 (s, 6H, Me), 1.80 (s, 6H, Me). Anal. Calcd for $C_{28}H_{32}N_4MgB_2F_8$: C, 54.00; H, 5.18; N, 9.00. Found: C, 53.73; H, 5.24; N, 8.79.

Synthesis of $[L^{\Delta}Mg]$. Li₂(diox)₅[LMg] (121 mg, 0.134 mmol) was dissolved in 3 mL of MeCN and added to powdered $[L^{\Delta\Delta}Mg](BF_4)_2$ (76 mg, 0.134 mmol). The resulting vermilion red solution was evaporated. The remaining solid residue was triturated in 3 mL of CH₂Cl₂ and the white salt was filtered off and the filtrate evaporated and dried to give 120 mg (100%) of crude material. Single crystals of X-ray quality were grown by vapor diffusion of toluene into a concentrated CH₂Cl₂ solution of the product that was spiked with MeCN; diffraction data showed that the acetonitrile adduct $[L^{\Delta}Mg(NCMe)]$ •CH₂Cl₂ was obtained.

Preparation of activated calcium. Calcium iodide (12.03 g, 40.93 mmol), naphthalene (10.49 g, 81.85 mmol, 2 equiv.) and lithium metal (0.568 g, 81.85 mmol, 2 equiv) were mixed in 100 mL THF and the mixture was stirred at room temperature overnight. The black suspension was filtered and dried under vacuum on the frit at room temperature. The solid was transferred to a high-vacuum flask and further dried overnight under 10 µTorr at 140 °C. Yield: 4.99 g (72%) of black Ca(C₁₀H₈)_{0.98}. Anal. Calcd for C_{9.80}H_{7.84}Ca: C, 71.07; H, 4.78; Ca, 24.15. Found: C, 71.08; H, 4.71; Ca, 24.37.

Synthesis of LCa₂(NCMe)₄. Activated calcium (1.94 g, 11.53 mmol) and LH₄ (2.47 g, 5.77 mmol, 0.5 equiv.) were mixed in THF and refluxed overnight. The colorless solution was cooled to room temperature, then cooled further to -80° C where the temperature of the solution was maintained for 2 hr. The white precipitate was filtered cold, dried, recrystallized from toluene

(100 mL)/MeCN (200 mL) and dried in vacuum. Yield: 1.02 g (27%). ¹H NMR (500 MHz, THF-d₈): $\delta = 5.89$ (s, 8H, pyrrole), 1.95 (s, 12H, MeCN), 1.31 (s, 24H, Me).

Synthesis of $[L^{AA}Ca](BF_4)_2$. A 5-mL toluene suspension of $LCa_2(NCMe)_4$ (0.48 g, 0.71 mmol) was added dropwise to a 20-mL MeCN solution of FcBF₄ (0.62 g, 2.28 mmol, 4 equiv). The resulting green solution was evaporated and dried under vacuum. The solid was triturated in 30 mL of CH₂Cl₂ for 20 min., filtered, and resuspended in 300 mL of CH₂Cl₂, which was then brought to reflux. The warm suspension was filtered and the product was precipitated from the filtrate by dropwise addition of 100 mL of hexanes. The white powder was filtered and dried in vacuum. Yield: 0.13 g (37%). ¹H NMR (500 MHz, CD₃CN): $\delta = 7.73$ (d, 5 Hz, 4H, pyrrole), 6.81 (d, 5 Hz, 4H, pyrrole), 2.00 (s, 6H, Me), 1.87 (s, 6H, Me), 1.80 (s, 6H, Me), 1.79 (s, 6H, Me). Anal. Calcd for $[L^{\Delta\Delta}Ca](BF_4)_2$ ·0.3CH₂Cl₂, C_{28.3}H_{32.6}N₄CaB₂F₈Cl_{0.6}: C, 51.19; H, 4.95; N, 8.44; Ca, 6.02. Found: C, 51.54; H, 4.82; N, 8.30; Ca, 6.08.

Synthesis of $[L^{A}Ca]$. A 5-mL MeCN suspension of $[L^{\Delta\Delta}Ca](BF_4)_2$ (90 mg, 0.13 mmol) was added to a 5-mL MeCN solution of $LCa_2(NCMe)_4$ (86 mg, 0.13 mmol) under stirring. The brown mixture was stirred for 10 min. at room temperature, then evaporated and dried in vacuum. The solid residue was triturated in 3 mL CH₂Cl₂ and filtered, then the filtrate was evaporated and dried. The compound decomposes in solution, but is reasonably stable as a solid for a few days. Its decomposition was monitored by UV-vis in dilute solution at room temperature, and under those conditions we observed a marked bleach of its spectrum overnight. Its solid-state stability is better, however after several days in the glovebox. In a regular vial (capped but not Teflonlined) the solid was found to be partly decomposed. Cooling it to -30 °C or even -80 °C only marginally improved its stability. This instability prevented us from obtaining X-ray quality crystals, which in our hands need to be grown extremely slowly for all of our metalloporphyrinogens (a week to several weeks). For purification, the recrystallization was performed quickly (carried out over a few hours) by liquid-liquid diffusion of pentane into a concentrated CH₂Cl₂ solution to yield a microcrystalline powder. Yield: 110 mg (88%). Anal. Calcd for [L^ΔCa]·0.18CH₂Cl₂, C_{28.18}H_{32.36}N₄CaCl_{0.36}: C, 70.55; H, 6.80; N, 11.69; Ca, 8.34. Found: C, 70.88; H, 6.46; N, 11.25; Ca, 8.26.

X-ray Crystal Structure of $[L^{\Delta}Mg(CH_{3}CN)]$ •CH₂Cl₂. A bright vermilion red crystal of 0.44 × 0.21 × 0.06 mm³ dimension was coated with Paratone N oil and mounted on a glass fiber. X-ray diffraction data were collected at -80 °C on a Siemens CCD diffractometer, using the Mo K α radiation, selected by a graphite monochromator. The data were integrated to *hkl*-intensity and the final unit cell calculated using the SAINT v.4.050 program from Siemens. Solution and refinement were performed with the SHELXTL v.5.03 suite of programs developed by G. M. Sheldrick and Siemens Industrial Automation, 1995. The structure was solved by direct methods; the least-squares refinement converged normally (with hydrogen atoms placed at calculated positions using a standard riding model and refined isotropically).

Physical Measurements. UV-vis solution absorption spectra were recorded on a Cary-17 spectrophotometer modified by On-Line Instrument Systems (OLIS) to include computer control, or a Spectral Instruments 440 Model spectrophotometer. NMR spectra were recorded at the MIT Department of Chemistry Instrumentation Facility (DCIF) on a Varian Inova-500 spectrometer at 20 °C.

Computational Methods. A single-point (SP) density functional theoretical (DFT) computation was performed on the atomic coordinates of the crystal structure using the Amsterdam Density Functional (ADF2002.02) program^{3,4} on a home-built Linux cluster comprising sixty Intel processors organized in groups of twelve running in parallel. The generalized gradient approximation was used as implemented in ADF by the Becke-88 functional for exchange,⁵ and the Perdew-Wang-91 functional for correlation.⁶ A basis set of triple- ζ Slater-type functions augmented by a polarization set (TZP) was used for Mg and N atoms and double- ζ with polarization (DZP) for other atoms, with frozen core approximation. Orbitals were visualized using the Windows or Linux version of the Molekel software.^{7,8}

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identification code	00325t
empirical formula	$C_{31}H_{37}Cl_2MgN_5$
formula weight	574.87
<i>T</i> (K)	193(2)
λ (Å)	0.71073
crystal system	Triclinic
space group	$P\overline{1}$
a (Å)	10.4274(7)
<i>b</i> (Å)	10.6231(7)
<i>c</i> (Å)	14.3549(10)
α (deg)	81.9710(10)
β (deg)	85.0730(10)
$\gamma(\text{deg})$	73.5010(10)
$V(\text{\AA}^3)$	1507.90(18)
Ζ	2
$ ho_{ m calcd} ({ m g cm}^{-3})$	1.266
crystal size (mm ³)	$0.44 \times 0.21 \times 0.08$
abs coeff (mm ^{-1})	0.265
<i>F</i> (000)	608
θ range for data collection	2.01 to 23.29°
limiting indices	$-11 \le h \le 10, -11 \le k \le 11, -15 \le \ell \le 15$
no. of reflns collcd	7845
no. of ind reflns (R_{int})	4327 (0.0504)
completeness to $\theta = 23.25^{\circ}$	99.7 %
absorption corr	none
refinement method	Full-matrix least-squares on F ²
data / restraints / parameters	4327 / 0 / 362
$R1$, ^a $wR2^b$ $[I > 2\sigma]$	0.0928, 0.2700
$R1$, ^a $wR2^b$ (all data)	0.1104, 0.2899
$\operatorname{GOF}^{\operatorname{c}}$ on F^2	1.028
extinction coefficient	0.0000(4)
largest diff. peak and hole	0.690 and $-1.222 \text{ e}\text{\AA}^{-3}$

Table S1. Crystal data, structure solution and refinement for $[L^{\Delta}Mg(CH_{3}CN)] \cdot CH_{2}Cl_{2}$.

^{*a*} $R1 = \Sigma ||F_o - |F_c|| / \Sigma |F_o|$. ^{*b*} $wR2 = (\Sigma (w(F_o^2 - F_c^2)^2) / \Sigma (w(F_o^2)^2))^{1/2}$. ^{*c*} GOF = $(\Sigma w(F_o^2 - F_c^2)^2 / (n - p))^{1/2}$ where *n* is the number of data and *p* is the number of parameters refined.



Figure S1. Atomic numbering scheme for the crystal structure of $[L^{\Delta}Mg(CH_3CN)] \cdot CH_2Cl_2$. The dichloromethane solvent molecule, which is not shown, is labeled with atoms C(31), Cl(1) and Cl(2).

Atom	Х	У	Z	U_{eq}^{a}
Mg(1)	816(2)	4450(2)	7424(1)	22(1)
N(1)	496(4)	6476(4)	6721(3)	25(1)
N(3)	916(4)	2489(4)	7342(3)	24(1)
N(4)	-1215(4)	4936(4)	7819(3)	25(1)
N(2)	2362(4)	4281(4)	6275(3)	25(1)
N(5)	1902(4)	4457(4)	8618(3)	33(1)
C(18)	-141(5)	1948(5)	7584(3)	26(1)
C(15)	1837(5)	1604(5)	6820(3)	25(1)
C(25)	-2120(5)	6156(5)	7654(3)	27(1)
C(11)	2827(5)	3214(5)	5866(3)	24(1)
C(22)	-1947(5)	4028(5)	7942(3)	24(1)
C(5)	2649(5)	6560(5)	5757(4)	31(1)
C(12)	3150(5)	1867(5)	6442(3)	28(1)
C(8)	2215(5)	5378(5)	5538(3)	26(1)
C(19)	-1292(5)	2560(5)	8245(3)	29(1)
C(4)	1154(5)	6658(5)	5806(3)	27(1)
C(3)	207(5)	7675(5)	5220(4)	33(1)
C(1)	-668(5)	7351(5)	6697(3)	26(1)
C(29)	2564(6)	4425(6)	9202(4)	35(1)
C(26)	-1657(5)	7413(5)	7536(4)	31(1)
C(9)	2509(5)	4848(5)	4642(4)	32(1)
C(16)	1366(5)	538(5)	6731(4)	30(1)
C(10)	2934(5)	3529(6)	4835(4)	32(1)
C(27)	-969(6)	7486(5)	8429(4)	36(1)
C(2)	-864(5)	8132(5)	5775(4)	34(1)
C(20)	-745(6)	2432(6)	9235(4)	38(1)
C(23)	-3297(5)	4675(5)	7839(3)	28(1)
C(13)	4044(5)	1883(5)	7240(4)	35(1)
C(14)	3943(5)	794(5)	5836(4)	35(1)
C(17)	110(5)	749(5)	7221(4)	31(1)
C(24)	-3409(5)	6031(5)	7654(3)	28(1)
C(28)	-2865(5)	8643(5)	7386(4)	39(1)
C(21)	-2353(6)	1816(6)	8324(4)	39(1)
C(6)	3366(5)	6452(6)	6646(4)	38(1)
C(7)	3155(6)	7354(6)	4912(4)	40(1)
C(30)	3428(8)	4381(9)	9952(5)	73(2)
Cl(2)	3401(7)	10525(6)	9676(3)	206(2)
C(31)	2518(9)	9830(10)	9083(6)	84(3)
Cl(1)	3575(5)	8234(4)	8781(3)	160(2)

Table S2. Atomic coordinates $(\times 10^4)$ and equivalent isotropic displacement parameters $(\text{\AA}^2 \times 10^3)$ for $[\text{L}^{\Delta}\text{Mg}(\text{CH}_3\text{CN})] \cdot \text{CH}_2\text{Cl}_2$.

 $^{a}\,U_{eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Bond	Distance	Bond	Distance
Mg(1)—N(3)	2.076(4)	C(22)—C(19)	1.530(7)
Mg(1)—N(4)	2.080(4)	C(5)—C(6)	1.508(7)
Mg(1)—N(5)	2.136(5)	C(5)—C(7)	1.523(7)
Mg(1)—N(1)	2.193(4)	C(5)—C(8)	1.528(7)
Mg(1)—N(2)	2.194(4)	C(5)—C(4)	1.529(7)
N(1)—C(1)	1.302(6)	C(12)—C(14)	1.536(7)
N(1)—C(4)	1.443(6)	C(12)—C(13)	1.543(7)
N(3)—C(18)	1.379(6)	C(8)—C(9)	1.450(7)
N(3)—C(15)	1.388(6)	C(8)—C(4)	1.562(7)
N(4)—C(25)	1.372(6)	C(19)—C(21)	1.521(7)
N(4)—C(22)	1.377(6)	C(19)—C(20)	1.551(7)
N(2)—C(11)	1.300(6)	C(4)—C(3)	1.460(7)
N(2)—C(8)	1.443(6)	C(3)—C(2)	1.328(8)
N(5)—C(29)	1.122(7)	C(1)—C(2)	1.458(7)
C(18)—C(17)	1.391(7)	C(1)—C(26)	1.513(7)
C(18)—C(19)	1.516(7)	C(29)—C(30)	1.449(8)
C(15)—C(16)	1.381(7)	C(26)—C(28)	1.541(7)
C(15)—C(12)	1.515(7)	C(26)—C(27)	1.543(7)
C(25)—C(24)	1.388(7)	C(9)—C(10)	1.340(8)
C(25)—C(26)	1.528(7)	C(16)—C(17)	1.406(8)
C(11)—C(10)	1.474(7)	C(23)—C(24)	1.400(7)
C(11)—C(12)	1.512(7)	Cl(2)—C(31)	1.678(11)
C(22)—C(23)	1.390(7)	C(31)—Cl(1)	1.826(11)

Table S3. Bond lengths (in Å) for $[L^{\Delta}Mg(CH_{3}CN)] \cdot CH_{2}Cl_{2}$.

Bond Angle	Bond Angle Angle		Angle
N(3)–Mg(1)–N(4)	93.25(16)	C(24)-C(25)-C(26)	128.9(5)
N(3)–Mg(1)–N(5)	106.58(17)	N(2)-C(11)-C(10)	111.2(4)
N(4)–Mg(1)–N(5)	108.27(17)	N(2)-C(11)-C(12)	120.6(4)
N(3)–Mg(1)–N(1)	148.64(17)	C(10)-C(11)-C(12)	128.2(4)
N(4)–Mg(1)–N(1)	87.89(16)	N(4)-C(22)-C(23)	109.7(4)
N(5)–Mg(1)–N(1)	102.75(17)	N(4)-C(22)-C(19)	121.3(4)
N(3)–Mg(1)–N(2)	87.13(16)	C(23)-C(22)-C(19)	128.6(4)
N(4)-Mg(1)-N(2)	147.59(17)	C(6)–C(5)–C(7)	114.1(4)
N(5)-Mg(1)-N(2)	102.61(17)	C(6)–C(5)–C(8)	119.5(4)
N(1)-Mg(1)-N(2)	75.77(15)	C(7)–C(5)–C(8)	115.6(4)
C(1)-N(1)-C(4)	106.4(4)	C(6)–C(5)–C(4)	120.3(4)
C(1)-N(1)-Mg(1)	123.5(3)	C(7)–C(5)–C(4)	116.0(4)
C(4)-N(1)-Mg(1)	117.7(3)	C(8)–C(5)–C(4)	61.4(3)
C(18)–N(3)–C(15)	106.0(4)	C(11)-C(12)-C(15)	107.7(4)
C(18)–N(3)–Mg(1)	123.9(3)	C(11)-C(12)-C(14)	110.8(4)
C(15)–N(3)–Mg(1)	127.9(3)	C(15)-C(12)-C(14)	110.6(4)
C(25)-N(4)-C(22)	106.2(4)	C(11)-C(12)-C(13)	108.3(4)
C(25)–N(4)–Mg(1)	126.6(3)	C(15)-C(12)-C(13)	111.9(4)
C(22)-N(4)-Mg(1)	122.9(3)	C(14)-C(12)-C(13)	107.6(4)
C(11)–N(2)–C(8)	106.4(4)	N(2)-C(8)-C(9)	108.0(4)
C(11)-N(2)-Mg(1)	122.5(3)	N(2)–C(8)–C(5)	116.3(4)
C(8)-N(2)-Mg(1)	117.5(3)	C(9)–C(8)–C(5)	123.6(4)
C(29)–N(5)–Mg(1)	174.4(4)	N(2)–C(8)–C(4)	113.0(4)
N(3)-C(18)-C(17)	110.0(4)	C(9)–C(8)–C(4)	129.7(4)
N(3)-C(18)-C(19)	121.8(4)	C(5)–C(8)–C(4)	59.3(3)
C(17)–C(18)–C(19)	127.9(5)	C(18)-C(19)-C(21)	110.1(4)
C(16)-C(15)-N(3)	110.4(4)	C(18)-C(19)-C(22)	113.4(4)
C(16)-C(15)-C(12)	128.8(5)	C(21)-C(19)-C(22)	108.9(4)
N(3)-C(15)-C(12)	120.8(4)	C(18)-C(19)-C(20)	108.3(4)
N(4)-C(25)-C(24)	110.6(4)	C(21)-C(19)-C(20)	108.1(4)
N(4)-C(25)-C(26)	120.4(4)	C(22)-C(19)-C(20)	107.8(4)

Table S4. Bond angles (in deg) for $[L^{\Delta}Mg(CH_3CN)] \cdot CH_2Cl_2$.

Table S4 cont'd

Bond Angle Angle		Bond Angle	Angle	
N(1)-C(4)-C(3)	107.5(4)	C(25)-C(26)-C(28)	110.2(4)	
N(1)-C(4)-C(5)	118.3(4)	C(1)-C(26)-C(27)	109.7(4)	
C(3)–C(4)–C(5)	122.2(4)	C(25)-C(26)-C(27)	109.7(4)	
N(1)-C(4)-C(8)	113.2(4)	C(28)–C(26)–C(27)	108.6(4)	
C(3)–C(4)–C(8)	129.9(4)	C(10)–C(9)–C(8)	106.9(4)	
C(5)–C(4)–C(8)	59.3(3)	C(15)-C(16)-C(17)	106.8(4)	
C(2)–C(3)–C(4)	106.6(5)	C(9)–C(10)–C(11)	107.1(5)	
N(1)-C(1)-C(2)	111.2(4)	C(3)–C(2)–C(1)	108.0(4)	
N(1)-C(1)-C(26)	120.9(4)	C(22)–C(23)–C(24)	107.2(4)	
C(2)–C(1)–C(26)	127.8(4)	C(18)–C(17)–C(16)	106.9(4)	
N(5)-C(29)-C(30)	179.5(7)	C(25)–C(24)–C(23)	106.2(4)	
C(1)-C(26)-C(25)	107.8(4)	Cl(2)–C(31)–Cl(1)	109.4(6)	
C(1)-C(26)-C(28)	110.7(4)			

Atom	U ₁₁	Um	IJ22	Um	U ₁₂	Ula
$M_{\alpha}(1)$	22(1)	22(1)	21(1)	1(1)	2(1)	9(1)
Mg(1)	23(1) 25(2)	23(1) 22(2)	21(1) 27(2)	1(1)	-3(1)	$-\delta(1)$
N(1) N(2)	23(2) 26(2)	23(2) 21(2)	$\frac{27(2)}{25(2)}$	0(2)	-3(2)	-9(2)
N(3) N(4)	20(2) 24(2)	21(2) 25(2)	23(2) 25(2)	2(2) 2(2)	0(2) 1(2)	-8(2)
N(4) N(2)	24(2) 25(2)	23(2) 25(2)	23(2) 25(2)	-3(2)	1(2) 2(2)	-7(2) 11(2)
N(2) N(5)	25(2) 36(3)	23(2) 37(3)	23(2) 27(2)	2(2) 2(2)	-3(2)	-11(2) 0(2)
$\Gamma(3)$	30(3)	$\frac{37(3)}{26(3)}$	$\frac{27(2)}{24(3)}$	-2(2)	-3(2)	-9(2)
C(10) C(15)	20(3) 27(3)	20(3) 24(3)	24(3) 23(3)	$\frac{3(2)}{1(2)}$	-2(2)	-9(2) 5(2)
C(15) C(25)	27(3) 26(3)	24(3) 30(3)	23(3)	$\frac{1(2)}{3(2)}$	-1(2)	-3(2)
C(23) C(11)	20(3) 20(2)	30(3)	25(3)	-3(2)	0(2)	-0(2) 10(2)
C(11) C(22)	20(2) 26(3)	20(3)	20(3)	-2(2)	0(2)	-10(2) 13(2)
C(22)	20(3)	29(3) 30(3)	20(2) 37(3)	-2(2)	-3(2)	-13(2) -13(2)
C(3)	20(3) 27(3)	30(3) 27(3)	$\frac{37(3)}{27(3)}$	-3(2)	-3(2)	-13(2) -4(2)
C(12)	27(3) 28(3)	27(3) 29(3)	27(3) 24(3)	-3(2)	1(2) 0(2)	-4(2) 14(2)
C(0)	20(3)	29(3)	24(3)	2(2) 2(2)	3(2)	-14(2) -13(2)
C(1)	28(3)	25(3)	20(3)	$\frac{2(2)}{6(2)}$	-5(2)	-13(2) -13(2)
C(4)	23(3)	20(3) 35(3)	$\frac{2}{3}(3)$	11(2)	-9(2)	-13(2) -18(2)
C(3)	27(3)	21(2)	32(3)	0(2)	-6(2)	-11(2)
C(29)	$\frac{27(3)}{37(3)}$	$\frac{21(2)}{41(3)}$	26(3)	-5(2)	-5(3)	-11(2) -11(3)
C(25)	30(3)	25(3)	36(3)	-1(2)	-5(2)	-7(2)
C(20)	34(3)	40(3)	23(3)	3(2)	-1(2)	-16(2)
C(16)	37(3)	21(3)	30(3)	-2(2)	-2(2)	-5(2)
C(10)	37(3)	42(3)	25(3)	-7(2)	2(2) 2(2)	-17(2)
C(27)	40(3)	31(3)	39(3)	-8(2)	-7(2)	-12(2)
C(2)	27(3)	27(3)	45(3)	11(2)	-14(2)	-8(2)
C(20)	45(3)	$\frac{27(3)}{38(3)}$	28(3)	4(2)	1(2)	-10(3)
C(23)	28(3)	37(3)	23(3)	-3(2)	1(2)	-17(2)
C(13)	27(3)	35(3)	38(3)	1(2)	-5(2)	-3(2)
C(14)	31(3)	29(3)	43(3)	-8(2)	3(2)	-6(2)
C(17)	39(3)	21(3)	34(3)	3(2)	-2(2)	-16(2)
C(24)	23(3)	35(3)	26(3)	-6(2)	-3(2)	-8(2)
C(28)	33(3)	29(3)	52(4)	-8(3)	-3(3)	-4(2)
C(21)	35(3)	34(3)	48(3)	2(3)	9(3)	-17(2)
Č(6)	32(3)	36(3)	48(3)	-4(3)	-7(2)	-14(2)
C(7)	37(3)	37(3)	48(3)	3(3)	3(3)	-20(3)
C(30)	70(5)	109(7)	48(4)	-10(4)	-30(4)	-30(5)
Cl(2)	309(7)	195(5)	110(3)	4(3)	9(4)	-80(5)
C(31)	77(6)	115(7)	50(5)	24(5)	-5(4)	-25(5)
Cl(1)	165(4)	153(3)	134(3)	-12(2)	15(3)	-10(3)

Table S5. Anisotropic thermal displacement parameters $(Å^2 \times 10^3)$ for $[L^{\Delta}Mg(CH_3CN)] \cdot CH_2Cl_2$.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^{*}b^{*}U_{12}]$.

Atom	Х	У	Z	U_{eq}
H(3)	333	7956	4569	40
H(9)	2417	5341	4035	38
H(16)	1805	-196	6403	36
H(10)	3247	2913	4390	39
H(27A)	-214	6695	8544	54
H(27B)	-1615	7535	8970	54
H(27C)	-642	8275	8341	54
H(2)	-1625	8843	5601	41
H(20A)	-357	1496	9458	57
H(20B)	-1478	2818	9674	57
H(20C)	-54	2902	9198	57
H(23)	-4009	4273	7886	34
H(13A)	4815	2188	6973	52
H(13B)	4357	988	7572	52
H(13C)	3526	2482	7684	52
H(14A)	3396	754	5325	52
H(14B)	4175	-64	6228	52
H(14C)	4765	1007	5569	52
H(17)	-459	181	7290	37
H(24)	-4208	6725	7550	33
H(28A)	-2551	9441	7284	58
H(28B)	-3479	8680	7944	58
H(28C)	-3331	8592	6834	58
H(21A)	-2687	1854	7700	58
H(21B)	-3096	2223	8749	58
H(21C)	-1961	891	8575	58
H(6A)	3289	7339	6803	56
H(6B)	4314	5981	6548	56
H(6C)	2962	5964	7163	56
H(7A)	2988	8272	5038	59
H(7B)	2684	7334	4354	59
H(7C)	4118	6968	4799	59
H(30A)	3899	3459	10162	109
H(30B)	2887	4786	10481	109
H(30C)	4083	4869	9719	109
H(31A)	2202	10417	8501	101
H(31B)	1726	9703	9475	101

Table S6. Hydrogen coordinates (×10⁴) and isotropic displacement parameters (Å² × 10³) for $[L^{\Delta}Mg(CH_{3}CN)] \cdot CH_{2}Cl_{2}$.

MO No.	Occup.	Energy (eV)	MO No.	Occup.	Energy (eV)
86	2.000	-6.540	96	0.000	-2.379
87	2.000	-6.431	97	0.000	-1.771
88	2.000	-6.267	98	0.000	-1.198
89	2.000	-6.067	99	0.000	-1.198
90	2.000	-6.043	100	0.000	-0.462
91	2.000	-5.401	101	0.000	0.333
92	2.000	-4.088	102	0.000	0.386
93	2.000	-3.932	103	0.000	0.708
94	2.000	-3.234	104	0.000	0.849
95	2.000	-3.103	105	0.000	0.939

Table S7. Energies of the frontier and near-frontier orbitals of $[L^{\Delta}Mg(CH_3CN)]$ according to the SP DFT (GGA Becke88x/PW91, TZ2P) calculation.

Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge
1Mg	1.2071	19C	0.2394	37H	0.3914	55H	0.3847
2N	-0.5044	20C	-0.2014	38H	0.3897	56H	0.3915
3N	-0.6007	21C	0.4031	39H	0.3902	57H	0.3439
4N	-0.6991	22C	0.2781	40H	0.3634	58H	0.3217
5N	-0.501	23C	0.3305	41H	0.2342	59H	0.3257
6N	-0.3113	24C	0.9641	42H	0.3438	60H	0.3259
7C	0.2916	25C	0.3394	43H	0.367	61H	0.3397
8C	0.2639	26C	0.9508	44H	0.3637	62H	0.3437
9C	0.3279	27C	0.2969	45H	0.3447	63H	0.3345
10C	0.3384	28C	0.9643	46H	0.341	64H	0.3297
11C	0.311	29C	0.9169	47H	0.2822	65H	0.1909
12C	0.0391	30C	0.2743	48H	0.3821	66H	0.2802
13C	-0.1985	31C	0.2603	49H	0.3621	67H	0.3429
14C	0.1897	32C	0.9153	50H	0.3512	68H	0.2941
15C	-0.1965	33C	0.9311	51H	0.2423	69H	0.1897
16C	0.186	34C	0.9308	52H	0.3293	70H	0.1921
17C	0.4082	35C	0.8926	53H	0.3196		
18C	0.3396	36C	0.6932	54H	0.3449		

Table S8. Atomic charges of $[L^{\Delta}Mg(CH_3CN)]$ according to the Mulliken population analysis, with atom numbering scheme used for calculation provided below.

