Table S1. Selected Bond Lengths (Å) and Angles (deg) in **2B**

Atom1–Atom2	**2B**
Ru2–N5	2.1159(14)
Ru2–N7	2.1244(19)
Ru2–S3	2.2477(13)
Ru2–S4	2.2578(14)
Ru2–Cl3	2.4147(7)
Ru2–Cl4	2.4069(7)
N5–N6	1.3442(19)
N7–N8	1.3459(19)
S3–O3	1.4850(14)
S4–O4	1.4841(13)
Atom1–Atom2–Atom3	
N5–Ru2–N7	86.34(6)
N5–Ru2–S3	176.36(4)
N5–Ru2–S4	88.09(5)
N7–Ru2–S3	91.86(5)
N7–Ru2–S4	173.90(4)
N5–Ru2–Cl3	88.75(4)
N5–Ru2–Cl4	88.72(4)
N7–Ru2–Cl3	89.35(4)
N7–Ru2–Cl4	88.96(5)
S3–Ru2–S4	93.83(3)
S3–Ru2–Cl3	94.40(3)
S3–Ru2–Cl4	88.09(3)
S4–Ru2–Cl3	88.05(3)
S4–Ru2–Cl4	93.39(3)
Cl3–Ru2–Cl4	177.038(15)
C34–S3–C33	98.57(11)
C35–S4–C36	98.64(10)
O3–S3–C34	106.56(10)
O3–S3–C33	106.67(9)

O4–S4–C35	106.75(9)
O4–S4–C36	106.10(8)

Table S2. Selected Bond Lengths (Å) and Angles (deg) in **1**·2dmso, **2A** and **3**

Atom1–Atom2	**1**·2dmso	**2A**	**3**
Ru1–N1	2.083(2)	2.1255(14)	2.1060(14)
Ru1–N3		2.1177(18)	2.0835(13)
Ru1–S1	2.2964(6)	2.2588(8)	2.2596(6)
Ru1–S2		2.2439(13)	2.2461(8)
Ru1–Cl1	2.4014(6)	2.4105(7)	2.4270(8)
Ru1–Cl2		2.4137(7)	2.4148(6)
N1–N2	1.360(3)	1.3574(18)	1.3587(19)
N3–N4		1.353(2)	1.3578(19)
S1–O1	1.482(2)	1.4845(13)	1.4816(13)
S2–O2		1.4812(12)	1.4944(13)
Atom1–Atom2–Atom3			
N1–Ru1–N1′	180.00(17)		
N1–Ru1–N3		84.91(6)	87.62(5)
N1–Ru1–S1	92.28(7)	172.29(4)	175.24(4)
N1–Ru1–S2		94.68(4)	89.21(4)
N3–Ru1–S1		87.97(5)	88.13(4)
N3–Ru1–S2		177.31(4)	95.86(4)
N1–Ru1–Cl1	90.08(7)	88.29(4)	86.16(4)
N1–Ru1–Cl2		88.97(4)	89.29(4)
N3–Ru1–Cl1		88.57(5)	88.94(5)
N3–Ru1–Cl2		89.01(5)	174.68(4)
S1–Ru1–S1′	180.00(4)		
S2–Ru1–S1		92.57(3)	93.35(2)
S1–Ru1–Cl1	88.48(2)	88.59(3)	91.63(2)
S1–Ru1–Cl2		93.86(3)	94.786(16)
S2–Ru1–Cl1		94.08(4)	173.195(15)
S2–Ru1–Cl2		88.32(4)	88.42(3)
Cl1–Ru1–Cl1′	180.00(4)		
Cl1–Ru1–Cl2		176.488(15)	86.54(3)
C8–S1–C9	99.97(17)		

C15–S1–C16		99.22(9)	
C17–S2–C18		99.11(10)	
C15–S1–C16			98.47(10)
C17–S2–C18			98.78(9)
O1–S1–C8	107.04(14)		
O1–S1–C9	105.79(15)		
O1–S1–C15		106.91(8)	
O1–S1–C16		105.99(9)	
O2–S2–C17		106.58(8)	
O2–S2–C18		105.90(9)	
O1–S1–C15			106.13(9)
O1–S1–C16			107.58(9)
O2–S2–C17			106.17(8)
O2–S2–C18			105.41(9)

Table S3. Selected Bond Angles (deg) in **4**·CH_3CN and **5**·H_2O.

Atom1–Atom2–Atom3	**4**·CH_3CN	**5**·H_2O
N1–Ru1–N3	77.26(7)	76.04(5)
N1–Ru1–N4	167.88(6)	
N3–Ru1–N4	90.77(7)	
N1–Ru1–S1	97.75(5)	95.79(4)
N1–Ru1–S2		171.35(3)
N3–Ru1–S1	174.86(5)	171.65(4)
N3–Ru1–S2		95.31(4)
N4–Ru1–S1	94.26(5)	
N1–Ru1–Cl1	91.73(5)	85.55(4)
N1–Ru1–Cl2	87.68(5)	89.36(4)
N3–Ru1–Cl1	88.18(5)	87.37(5)
N3–Ru1–Cl2	89.57(5)	89.07(5)
N4–Ru1–Cl1	89.79(6)	
N4–Ru1–Cl2	90.33(6)	
S1–Ru1–S2		92.85(2)
S1–Ru1–Cl1	90.74(2)	90.31(3)
S1–Ru1–Cl2	91.50(2)	92.60(3)
S2–Ru1–Cl1		94.04(2)
S2–Ru1–Cl2		90.63(2)
Cl1–Ru1–Cl2	177.743(19)	174.373(13)
Ru1–N1–N2	113.35(11)	112.82(9)
Ru1–N3–C9	117.72(13)	118.84(11)
C10–S1–C11		99.96(9)
C12–S2–C13		99.33(10)
C17–S1–C18	98.97(11)	
O1–S1–C10		105.69(8)
O1–S1–C11		105.06(8)
O2–S2–C12		105.36(9)
O2–S2–C13		105.59(8)

O1–S1–C17	105.19(10)	
O1–S1–C18	104.95(10)	
N1–N2–C9	116.05(15)	116.31(12)
N2–C9–C8	118.63(17)	119.05(13)
N2–C9–N3	115.43(17)	115.72(13)

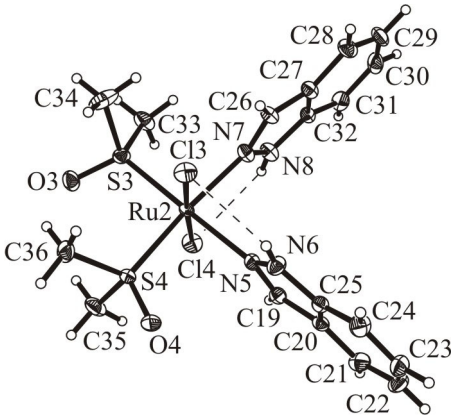

Fig. S1. Molecular structure of the second independent molecule of *trans*,*cis*,*cis*–[$RuCl_2(dmso)_2(Hind)_2$] (**2B**), showing the atom-numbering scheme. Thermal ellipsoids are drawn at 50% probability level.

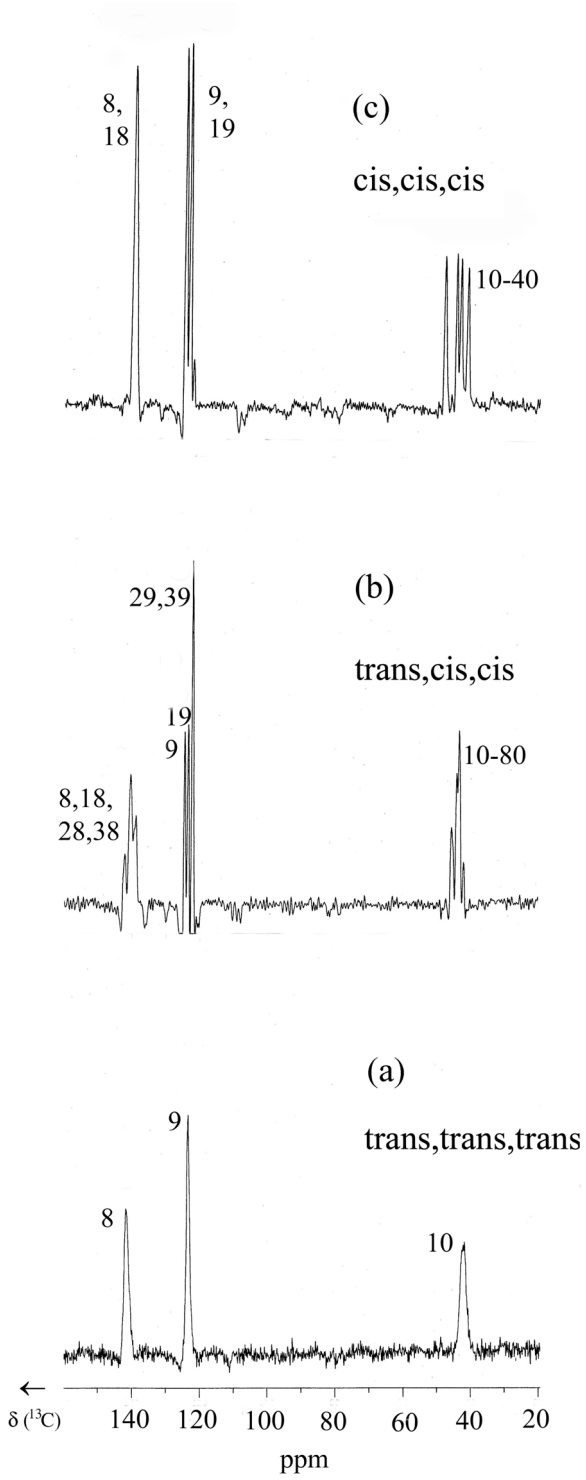

Fig. S2. ^{13}C CP MAS NMR TOSSNQS spectra of **1** (trace a), **2** (trace b), and **3** (trace c) at room temperature. Only signals of quaternary carbon atoms and methyl groups appeared in the spectra taken with this technique. Small signals in trace c result from non-perfect suppression of spin side bands during TOSS-sequence. Spectra in trace b and trace c have been subjected to Gauss multiplication prior to FT for an improved resolution. For atom labels see Fig. 6.

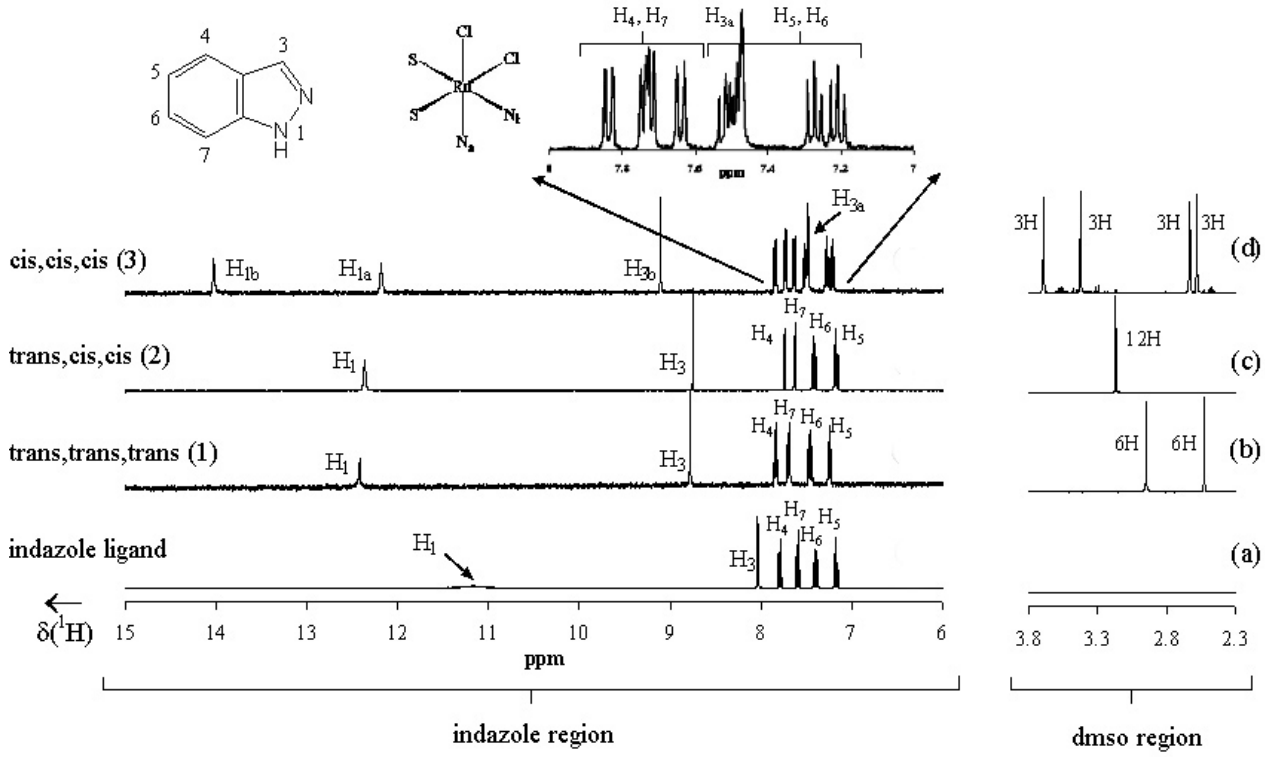

Fig. S3. ^{1}H NMR spectra in CD_3CN of the free ligand (a), *trans,trans,trans*-[$RuCl_2$(dmso)$_2$(Hind)$_2$] (b), *trans,cis,cis*-[$RuCl_2$(dmso)$_2$(Hind)$_2$] (c), and *cis,cis,cis*-[$RuCl_2$(dmso)$_2$(Hind)$_2$] (d).

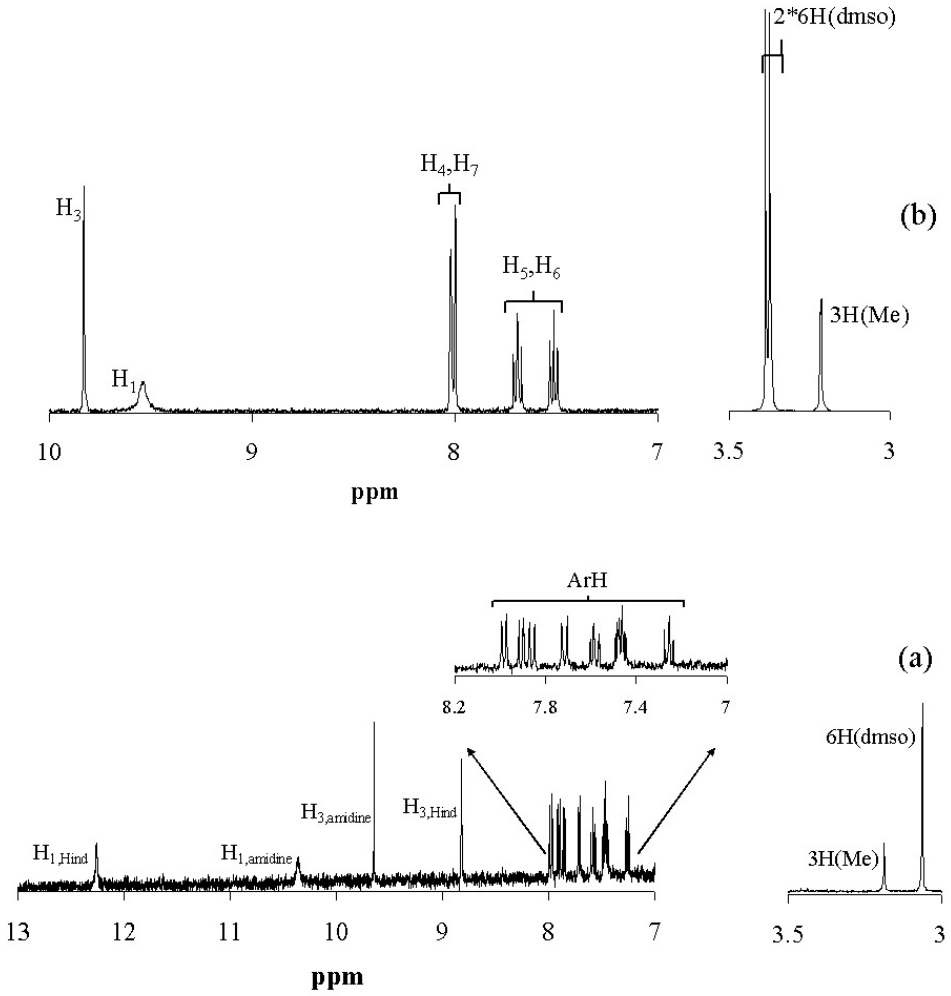

Fig. S4. ^{1}H NMR spectra of (a) *trans*-[$RuCl_2$(dm<u>s</u>o)(Hind){HN=C(Me)ind}]·CH_3CN (**4**·CH_3CN) and (b) *trans*,*cis*–[$Ru^{II}Cl_2$(dm<u>s</u>o)$_2$ {HN=C(Me)ind}]·H_2O (**5**·H_2O) in CD_3CN.

***cis,fac*-[RuCl$_2$(dm$\underline{s}$o)$_3$(Hind)].** Indazole (0.13 g, 1.06 mmol) was added to *cis*-[RuCl$_2$(dmso)$_4$] (0.50 g; 1.03 mmol) in methanol (25 ml). The yellow suspension was stirred overnight, filtered off, washed with cold methanol (3 × 3 ml), diethyl ether (2 × 3 ml) and dried *in vacuo* (0.31 g, 58 %). Found: C, 29.81; H, 4.51; N, 5.34; S, 18.39; Cl, 13.13. $C_{13}H_{24}Cl_2N_2O_3RuS_3$ requires C, 29.77; H, 4.61; N, 5.34; S, 18.34; Cl, 13.52. *m/z* (MeOH), negative: 447, $[M–dmso–H]^-$; positive: 549, $[M+Na]^+$; 471, $[M+Na–dmso]^+$; 431, $[M+Na–Hind]^+$. δ_H (400.13 MHz; solvent d_6-dmso) 13.68 (1H, s, H_1), 8.97 (1H, s, H_3); 7.87 (1H, d, J = 8.2 Hz, H_4); 7.77 (1H, d, J = 8.4 Hz, H_7); 7.46 (1H, t, J = 7.7 Hz, H_6); 7.21 (1H, t, J = 7.5 Hz, H_5); 3.46 (6H, s, H_{Me}); 3.44 (6H, s, H_{Me}); 3.14 (6H, s, H_{Me}). Single crystals suitable for X-ray diffraction study were grown by slow diffusion of hexane into a THF solution of the complex under protection of light.

Crystal data for *cis,fac*–[RuCl$_2$(dm$\underline{s}$o)$_3$(Hind)]: $C_{13}H_{24}Cl_2N_2O_3RuS_3$, M = 524.49 g/mol, monoclinic, space group P2(1)/n, a = 18.106(4), b = 9.167(2), c = 25.495(5) Å, β = 110.67(3)º, V = 3959.2(15) Å^3, Z = 8, D_c = 1.760 g/cm^3, μ(Mo-Kα) = 1.393 mm^{-1}, F(000) = 2128, Crystal size = 0.23 x 0.17 x 0.11 mm, Final R1 = 0.0278, wR2 = 0.0701, GOF = 1.036.

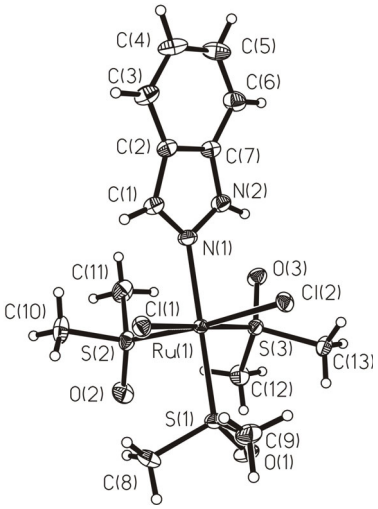

Fig. S5. Molecular structure of the first independent molecule of *cis,fac*–[RuCl$_2$(dm$\underline{s}$o)$_3$(Hind)], showing the atom-numbering scheme. Thermal ellipsoids are drawn at 50% probability level.

Table S4. Selected Bond Distances (Å) in *cis,fac*–[RuCl$_2$(dm$\underline{s}$o)$_3$(Hind)]:

Atom1–Atom2		Atom1–Atom2	
Ru1–N1	2.1475(16)	Ru2–N3	2.1273(16)
Ru1–S2	2.2593(9)	Ru2–S5	2.2629(7)
Ru1–S3	2.2796(6)	Ru2–S6	2.2915(10)
Ru1–S1	2.2934(6)	Ru2–S4	2.2979(6)
Ru1–Cl2	2.4181(9)	Ru2–Cl4	2.4209(7)

Ru1–Cl1	2.4396(6)	Ru2–Cl3	2.4305(10)
S1–O1	1.4829(15)	S2–O2	1.4816(16)

Synthesis of *cis,fac*-[$RuCl_2(dmso)_3(MeCN)$]

$[RuCl_2(dmso)_3L]$ (L = dmso, Hind) $\xrightarrow[RT]{MeCN}$ $[RuCl_2(dmso)_3(MeCN)]$

The complex *cis,fac*-[$RuCl_2(dmso)_3(MeCN)$] was prepared from *cis,fac*-[$RuCl_2(dmso)_3(Hind)$] in acetonitrile at room temperature as described in the literature (P.M.T. Piggot, L.A. Hall, A.J.P. White, D.J. Williams, *Inorg. Chim. Acta* 2004, **357**, 250-258).

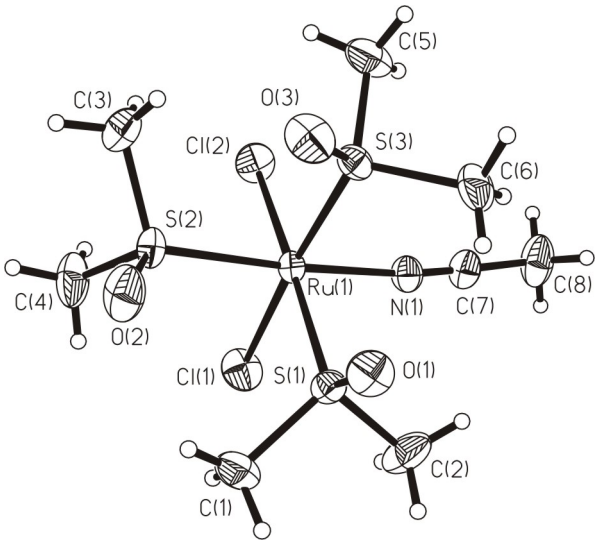

Fig. S6. Molecular structure of the *cis,fac*-[$RuCl_2(dmso)_3(MeCN)$], showing the atom-numbering scheme. Thermal ellipsoids are drawn at 50% probability level.

Optimized Cartesian Coordinates for Gas-Phase Structures of Isomers 1–3 (from DFT calculations)

1

C -2.477819 2.543697 0.719386
N -1.930581 1.316290 0.947222
N -1.192337 0.912102 -0.127475
C -1.288422 1.852879 -1.063974
C -2.095477 2.923993 -0.594598
C -3.281882 3.363832 1.530884
C -3.692435 4.569371 0.987279
C -3.326545 4.963677 -0.325206
C -2.535103 4.156123 -1.122015
Ru -0.135967 -0.930113 -0.177799
N 1.689489 0.197823 -0.080835
N 2.810384 -0.337763 -0.616914
C 3.840517 0.550569 -0.597040
C 3.335082 1.737328 0.000391
C 1.976825 1.440775 0.294341
C 5.171915 0.442617 -1.036528
C 5.979148 1.552623 -0.858595
C 5.494133 2.745317 -0.262623
C 4.184254 2.851079 0.167662
Cl 0.072236 -0.673594 -2.620926
Cl 1.238088 -2.985299 -0.314962
S -2.082480 -2.099355 -0.566703
C -1.795856 -3.486345 -1.684033
S -0.162247 -1.235914 2.090799
C 1.510593 -1.192195 2.776573
O -2.887931 -2.601326 0.577813
C -3.218403 -1.139069 -1.593682
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H 1.435144 -1.395831 3.847689
H 2.115370 -1.941506 2.261553

2

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C -2.440314 2.753161 -0.751295
C -3.306142 3.465693 1.453631
C -3.927560 4.520159 0.806852
C -3.819370 4.708428 -0.594479
C -3.084148 3.838595 -1.379432
Ru -0.136488 -0.900564 0.005680
N 1.600807 0.378695 0.163034
N 2.237291 0.812018 -0.957616
C 3.223282 1.701241 -0.649852
C 3.226679 1.820477 0.765775

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C 5.044135 3.374841 0.593142	H -1.601435 -3.968525 1.142002	S -0.121694 -2.338679 0.217829
C 4.158532 2.673714 1.391722	H -3.384801 -3.712301 0.948326	C -1.378112 -3.026368 -0.889612
Cl 0.150345 -0.852885 -2.462006	H -2.006474 -2.603182 -2.497929	Cl 0.214407 -0.342092 -2.440565
Cl -0.404046 -0.801436 2.467768	H -3.121842 -3.696965 -1.601798	N 2.098460 -0.064933 0.166949
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S 1.137975 -2.790945 0.164697	H 2.759975 -1.921078 1.713189	C 4.261375 -0.186051 0.788446
C 2.480068 -2.822804 -1.048598	H 2.757660 -3.726626 1.635838	C 2.903811 -0.261003 1.206695
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C 2.144478 -2.822244 1.667844		C 5.515509 -0.308332 1.421510
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H -1.691322 0.983030 1.846280	**3**	C 1.377931 3.026394 0.889873
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