Electronic Supplementary Information

For

A Dinuclear Platinum Complex Featuring the Diboran(4)-1,2-diyl Ligand in a μ_2-Bridging Coordination Mode

Holger Braunschweig,* Rüdiger Bertermann, Alexander Damme, and Thomas Kupfer

Institut für Anorganische Chemie

Julius-Maximilians Universität Würzburg

Am Hubland, 97074 Würzburg (Germany)

Fax: (+49)931-31-84623

E-mail: h.braunschweig@mail.uni-wuerzburg.de

Homepage: http://www-anorganik.chemie.uni-wuerzburg.de/Braunschweig/

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Experimental Section

General Procedure:

All manipulations were conducted either under an atmosphere of dry argon or *in vacuo* using standard Schlenk line or glovebox techniques. Solvents were purified by distillation from Na/K alloy under dry argon immediately prior to use. C_7D_8 and CD_2Cl_2 were degassed by three freeze-pump-thaw cycles and stored over molecular sieves. $[Pt(PEt_3)_4]$[1] and $I_2B_2(NMe_2)_2$[2] were prepared according to published procedures. NMR spectra were acquired on Bruker Avance 400 (^{1}H: 400.1 MHz, ^{11}B: 128.3 MHz, ^{13}C: 100.6 MHz, ^{31}P: 161.9 MHz) and Bruker Avance 500 (^{1}H: 500.1 MHz; ^{11}B: 160.4 MHz; ^{13}C: 125.7 MHz; ^{31}P: 202.4 MHz) FT-NMR spectrometers. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to external TMS *via* the residual protons of the solvent (^{1}H) or the solvent itself (^{13}C). ^{11}B NMR spectra were referenced to external $BF_3{\cdot}OEt_2$ and ^{31}P{^{1}H} NMR spectra to 85% H_3PO_4. Assignment of the ^{13}C NMR spectroscopic data was supported by DEPT 135 experiments and ^{13}C,^{1}H correlation experiments. Solid-state ^{31}P VACP/MAS NMR spectra were recorded by using a Bruker DSX-400 (^{13}C: 100.6 MHz, ^{31}P, 161.9 MHz; spinning rate, ^{13}C: 11 kHz, ^{31}P: 15 kHz) FT-NMR spectrometer with bottom layer rotors of ZrO_2 (diameter 4 mm) containing ca. 50 mg of sample. Chemical shifts were calibrated externally on adamantane.[3] Microanalyses (C, H, N) were performed on a Leco Instruments elemental analyzer, type CHNS 932.

Synthesis of 1:

$[Pt(PEt_3)_4]$ (372 mg, 0.55 mmol) was placed in a Schlenk flask and heated at 60 °C over a period of 1 h under high vacuum. Thus, one PEt_3 is removed to afford $[Pt(PEt_3)_3]$ as an orange oil. $I_2B_2(NMe_2)_2$ (101 mg, 0.27 mmol) was added at room temperature and the mixture was subsequently dissolved in mesitylene (2 mL) and heated at 165 °C for 10 minutes during which time the solution turned red in color. The solution was cooled to -30 °C and vacuum was applied for 5 minutes to remove free PEt_3. The red solution was stored in a glovebox over night at -25 °C to afford **1** (103 mg, 0.08 mol, 30%) as colorless crystals, which were washed with pentane and dried under reduced pressure. Crystals suitable for X-ray diffraction were obtained by crystallization from mesitylene at -25 °C.

NMR (room temperature):

*ISOMERIC MIXTURE --- ISOMER **1a** (62%)*

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300 K): δ = 3.98 (s, 6H; NCH_3), 3.42 (s, 6H; NCH_3), 2.38−1.82 (m, 24H; PCH_2), 1.13 ppm (m, 36H; PCH_2CH_3); ^{11}B NMR (128.3 MHz, CD_2Cl_2, 300 K): δ = 56.0 ppm; ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6, 300 K): δ = 55.3 (s; NCH_3), 49.2 (s; NCH_3), 17.9 (s; PCH_2), 8.73 ppm (s; $P(CH_2CH_3)_3$); ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2, 300 K): δ = 6.53 ppm ($^1J_{P-Pt}$ = 3413Hz).

*ISOMER **1b** (38%)*

^{1}H NMR (400.1 MHz, CD_2Cl_2, 300 K): δ = 3.21 (br s, 3H; NCH_3), 2.88 (s, 3H; NCH_3), 2.73 (br s, 3H; NCH_3), 2.59 (br s, 3H; NCH_3), 2.38−1.82 (m, 24H; PCH_2), 1.13 ppm (m, 36H; PCH_2CH_3); ^{11}B NMR (128.3 MHz, CD_2Cl_2, 300 K): δ = 56.0 ppm; ^{13}C DEPT135 NMR (125.7 MHz, C_6D_2, 345 K): δ = 42.0 (s; NCH_3), 18.8 (s; PCH_2), 8.94 ppm (s; $P(CH_2CH_3)_3$); ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2, 300 K): δ = 5.36 ppm ($^1J_{P-Pt}$ = 3230Hz).

NMR DATA OF BOTH ISOMERS in C_7D_8

$^{11}B\{^1H\}$ NMR (160.4 MHz, C_7D_8, 300 K): δ = 55.6 ppm (s vbr, *B*Pt); $^{31}P\{^1H\}$ NMR (202.4 MHz, C_7D_8, 300 K): δ = 6.40 (s, $^1J_{P-Pt}$ = 3417 Hz, *FWHM* = 27.5 Hz, 62% **1a**), 5.33 ppm (s, $^1J_{P-Pt}$ = 3238 Hz, *FWHM* = 48.4 Hz, 38% **1b**).

*SOLID STATE NMR **1***

$^{13}C\{^1H\}$ VACP/MAS NMR (300 K): δ = 56.8 (s, N*C*H_3), 51.1 (s, N*C*H_3), 22.4 (s, P*C*H_2), 21.2 (s, P*C*H_2), 19.4 (s, P*C*H_2), 16.2 (s, P*C*H_2), 15.5 (s, P*C*H_2), 9.58 (m, PCH_2CH_3), 7.73 (m, PCH_2CH_3); ^{31}P VACP/MAS NMR (300 K): δ = 12.75 (d, $^1J_{P-Pt}$ = 3416 Hz, $^2J_{P-P}$ = 326 Hz, P^1Et_3), 7.32 (d, $^1J_{P-Pt}$ = 3412 Hz, $^2J_{P-P}$ = 326 Hz, P^2Et_3) ppm.

El. Anal. (%) calc. for $C_{28}H_{72}B_2I_2P_4Pt_2$: C 27.42, H 5.92, N 2.28; found: C 27.91, H 5.93, N 2.26.
M.P.: 174.5 °C.

Synthesis of 2:

$[Pt(PEt_3)_4]$ (104 mg, 0.155 mmol) and $I_2B_2(NMe_2)_2$ (55.0 mg, 0.151 mmol) were dissolved in benzene (1.5 mL) and the solution stirred for 10 min at room temperature. All volatile were removed under reduced pressure and the oily residue was crystallized from toluene/pentane (1:1) at -25 °C. Analytically pure **2** (47.3 mg, 0.059 mmol, 39%) was isolated as orange crystals, which were washed with pentane (0.5 mL) and dried under reduced pressure.

^1H NMR(400.1 MHz, C_6D_6, 300 K): δ = 2.94 (s, 6 H, NCH_3), 2.73 (s, 3 H, NCH_3), 2.57 (s, 3 H, NCH_3), 2.34-2.18 (m, 6 H, PCH_2), 2.02-1.82 (m, 6 H, PCH_2), 1.07-0.95 ppm (m, 18 H, $P(CH_2CH_3)_3$); $^{11}B\{^1H\}$ NMR (C_6D_6, 128.3 MHz, 300 K): δ = 57.5 (br s, *B*I), 39.6 ppm (br s, *B*Pt); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 300 K): δ = 49.4 (s, $^3J_{C-Pt}$ = 109.9 Hz, *C*H_3), 47.8 (s, *C*H_3), 45.5 (s, $^3J_{C-Pt}$ = 60.6 Hz, *C*H_3), 44.1 (s, *C*H_3),), 18.7 (t, $^1J_{C-P}$ = 17.1 Hz, P*C*H_2), 8.96 ppm (t, $^2J_{C-P}$ = 15.7 Hz, PCH_2CH_3); $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 300 K): δ = 11.6 ppm (s, $^1J_{P-Pt}$ = 3066 Hz); El. Anal. (%) calc. for $C_{16}H_{42}B_2I_2N_2P_2Pt$: C 24.17, H 5.33, N 3.52; found: C 24.55, H 5.41, N 3.60.

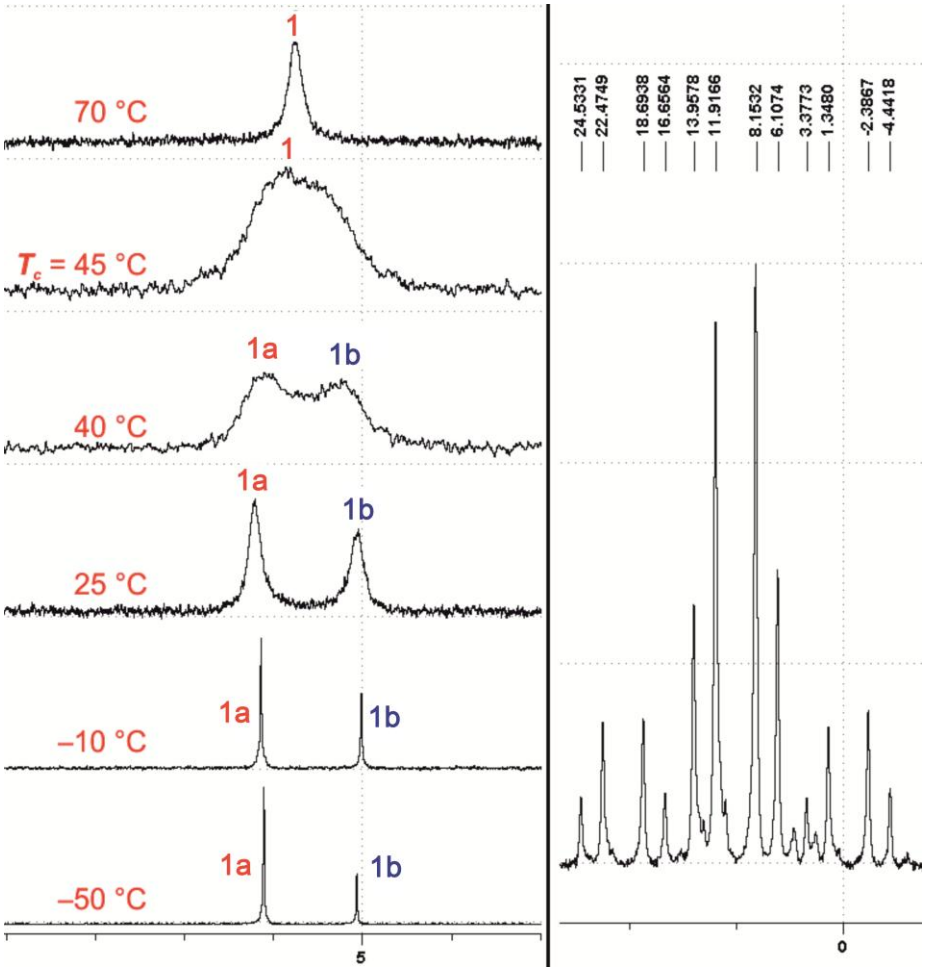


Figure S1. VT ^{31}P NMR spectroscopy on **1** between -50 °C and 70 °C (left; T_c = coalescence temperature) and AB-spin-system evident in the ^{31}P VPAC/MAS NMR spectrum of **1** in the solid state (right).

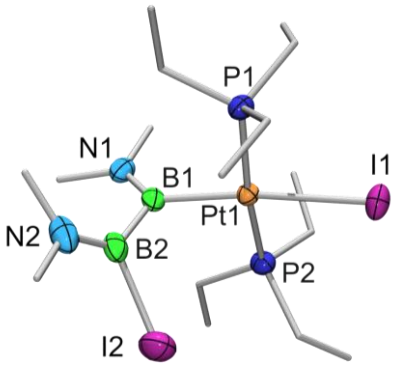
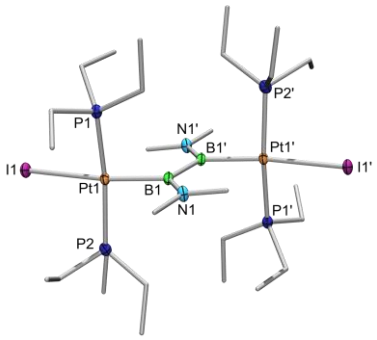


Figure S2. Molecular structure of **2** in the solid state. For clarity, hydrogen atoms and thermal ellipsoids of the carbon atoms have been removed.

Crystal Structure Determinations of 1 and 2

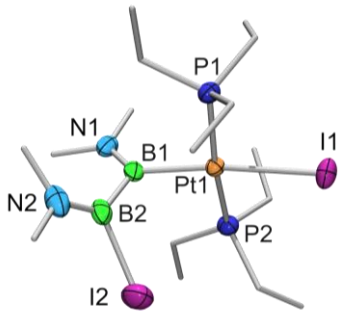
The crystal data of **1** and **2** were collected on a Bruker X8APEX diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using direct methods, refined with the Shelx software package (G. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112–122) and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factors calculations. All hydrogen atoms were assigned to idealized geometric positions. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-898500 (**1**) and CCDC-898501 (**2**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Crystal data for 1:



Data	**CCDC-898500**
Empirical formula	$C_{28}H_{72}B_2I_2N_2P_4Pt_2$
Formula weight ($g \cdot mol^{-1}$)	1226.36
Temperature (K)	100(2)
Radiation, λ (Å)	$Mo_{K\alpha}$ 0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	13.2082(13)
b (Å)	10.3273(11)
c (Å)	15.977(3)
α (°)	90.00
β (°)	99.482(5)
γ (°)	90.00
Volume ($Å^3$)	2149.6(5)
Z	2
Calculated density ($Mg \cdot m^{-3}$)	1.895
Absorbtion coefficient (mm^{-1})	8.106
F(000)	1172
Theta range for collection	1.86 to 26.74°
Reflections collected	49819
Independent reflections	4560
Minimum/maximum transmission	0.3076/0.7454
Refinement method	Full-matrix least-squares on F^2
Data / parameters / restrains	4560 / 183 / 0
Goodness-of-fit on F^2	1.078
Final R indices [I>2σ(I)]	R_1 = 0.0191, wR^2 = 0.0466
R indices (all data)	R_1 = 0.0235, wR^2 = 0.0487
Maximum/minimum residual electron density ($e \cdot Å^{-3}$)	1.352 / –0.785

Crystal data for 2:



Data	**CCDC-898501**
Empirical formula	$C_{16}H_{42}B_2I_2N_2P_2Pt$
Formula weight ($g \cdot mol^{-1}$)	794.96
Temperature (K)	173(2)
Radiation, λ (Å)	$Mo_{K\alpha}$ 0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	16.868(15)
b (Å)	11.209(10)
c (Å)	16.361(14)
α (°)	90.00
β (°)	113.295(10)
γ (°)	90.00
Volume ($Å^3$)	2841(4)
Z	4
Calculated density ($Mg \cdot m^{-3}$)	1.858
Absorbtion coefficient (mm^{-1})	7.238
F(000)	1504.0
Theta range for collection	1.31 to 26.06°
Reflections collected	27485
Independent reflections	5550
Minimum/maximum transmission	0.4823/0.7453
Refinement method	Full-matrix least-squares on F^2
Data / parameters / restrains	5550 / 230 / 0
Goodness-of-fit on F^2	1.133
Final R indices [I>2σ(I)]	R_1 = 0.0374, wR^2 = 0.0767
R indices (all data)	R_1 = 0.0443, wR^2 = 0.0793
Maximum/minimum residual electron density ($e \cdot Å^{-3}$)	1.392 / –0.893

Computational Details

The geometries of the **1a$_{calc}$** and **1b$_{calc}$** were fully optimized without symmetry restraints using Turbomole 5.10.[4] Subsequent single point calculations were conducted with the Gaussian09 program package.[5] The computations were performed using DFT methods, applying the three hybrid functional B3LYP using 6-31G** basis sets for H, B, C, P and N, 6-311G** basis sets for I[6] and Stuttgart relativistic, small core ECP basis sets for Pt.[7] Frequency calculations were used to verify that the final geometries represent energy minima. The transition state **1$_{TS}$** was localized applying the *Synchronous-Guided Quasi-Newton* method embedded within the Gaussian09 software package (QST2 option),[8,9] while the nature of the transition state was further verified by frequency calculations.

Cartesian coordinates:

1a$_{calc}$				**1b$_{calc}$**				**1$_{TS}$**			
Pt	-0.116184	-0.255333	-2.573597	Pt	0.467453	0.422612	-2.161464	Pt	2.262860	-0.477922	-0.481668
Pt	-0.016074	0.209597	2.575029	Pt	-0.254501	0.623271	2.106788	I	4.452022	-2.280832	0.217805
I	-0.133016	1.264180	-5.089999	I	-0.030609	2.573804	-4.076254	B	0.563482	0.694077	-0.655484
I	0.000867	-1.309543	5.091680	I	0.286551	2.910350	3.842545	N	0.353594	1.474123	-1.820853
P	2.188296	-0.539322	-2.799134	P	2.252887	1.664814	-1.285582	P	1.426747	-2.053046	-2.001711
P	-2.320578	0.493424	2.800458	P	1.096307	-0.687744	3.496101	C	-0.260696	-1.843552	-2.713308
P	2.306242	0.386660	2.703896	P	-2.006185	1.831336	1.121156	C	1.431930	-3.832750	-1.526574
P	-2.438473	-0.432522	-2.702604	P	-0.916880	-0.967760	-3.435617	C	2.512999	-2.044585	-3.493712
B	-0.087037	-0.707068	-0.550668	B	0.620998	-0.974269	-0.641440	P	3.424146	1.258518	0.566434
B	-0.045168	0.661242	0.552058	B	-0.444368	-0.897373	0.714389	C	3.673411	1.071049	2.383768
N	-0.098884	-2.013804	-0.027931	N	1.575855	-2.022188	-0.717939	C	5.136484	1.464346	-0.083333
N	-0.033363	1.967979	0.029344	N	-1.429004	-1.906745	0.880855	C	2.792366	2.991800	0.407871
C	2.827826	1.238146	4.253067	C	0.290371	-0.890563	5.141895	B	-0.564802	0.690150	0.653236
H	2.435817	0.684295	5.108269	H	0.921936	-1.477769	5.816683	N	-0.353664	1.461534	1.824134
H	3.919676	1.299424	4.310613	H	0.112842	0.100660	5.564835	Pt	-2.265854	-0.478159	0.471115
H	2.406889	2.246846	4.269891	H	-0.672277	-1.393192	5.016900	I	-4.457537	-2.272760	-0.241207
C	3.209259	1.366549	1.424298	C	2.775822	-0.059034	3.926233	P	-3.424537	1.267175	-0.564987
H	3.050476	0.936724	0.433994	H	2.685103	0.966161	4.290707	C	-2.790220	2.998381	-0.394389
H	2.821963	2.388046	1.409388	H	3.236888	-0.690595	4.692576	C	-3.674269	1.092633	-2.383534
H	4.281986	1.390841	1.641098	H	3.407877	-0.059028	3.034582	C	-5.136479	1.470996	0.086434
C	3.245545	-1.198756	2.749788	C	1.472034	-2.434423	3.020397	P	-1.432568	-2.064213	1.981404
H	4.314203	-1.019276	2.905842	H	0.547307	-2.959974	2.772932	C	-1.443778	-3.841489	1.497289
H	2.847291	-1.807760	3.564776	H	2.117182	-2.431410	2.137832	C	-2.517197	-2.060295	3.474635
H	3.102564	-1.740503	1.811229	H	1.986345	-2.957251	3.832862	C	0.256277	-1.863499	2.692215
C	3.197085	1.001225	-2.886600	C	1.932191	3.398463	-0.757092	H	1.008275	1.500574	-2.589465
H	4.248556	0.772729	-3.088668	H	1.378100	3.920108	-1.539813	H	-0.459047	2.054212	-1.977203
H	2.792606	1.629229	-3.683905	H	1.348843	3.391965	0.166830	H	-0.470779	-2.635224	-3.439342
H	3.120512	1.547875	-1.943100	H	2.880422	3.912639	-0.569560	H	-0.333426	-0.870209	-3.202110
C	3.100430	-1.560479	-1.558665	C	3.184460	1.012655	0.164280	H	-1.010576	-1.873864	-1.916233
H	3.009545	-1.122006	-0.563609	H	3.517203	-0.009617	-0.026872	H	2.426713	-4.104452	-1.168980
H	2.665473	-2.562033	-1.522062	H	4.047562	1.650168	0.380796	H	1.153299	-4.452609	-2.384676
H	4.159472	-1.637073	-1.824980	H	2.511368	1.009599	1.026205	H	0.716792	-4.003337	-0.720337
C	2.603854	-1.412631	-4.368127	C	3.566226	1.838417	-2.569034	H	3.534632	-2.274743	-3.182652
H	2.200669	-0.841371	-5.206499	H	3.138524	2.327642	-3.446642	H	2.503893	-1.052780	-3.952892
H	3.688342	-1.522893	-4.472469	H	4.404214	2.428254	-2.183062	H	2.172738	-2.784615	-4.225622
H	2.137826	-2.401456	-4.365383	H	3.925725	0.848516	-2.862392	H	4.293835	1.878727	2.785542
C	-2.959934	-1.283832	-4.251912	C	-0.125536	-1.316178	-5.063939	H	4.156730	0.107578	2.562479
H	-4.051781	-1.345078	-4.309541	H	-0.771440	-1.944592	-5.685977	H	2.704305	1.069837	2.889913
H	-2.567852	-0.729896	-5.107025	H	0.065627	-0.365220	-5.565947	H	5.651946	2.275348	0.441768
H	-2.539022	-2.292543	-4.268822	H	0.829503	-1.823470	-4.904239	H	5.090682	1.695345	-1.150882
C	-3.341523	-1.412608	-1.423176	C	-2.586370	-0.341403	-3.906358	H	5.678566	0.525686	0.043454
H	-2.953930	-2.433987	-1.408061	H	-2.477417	0.648633	-4.353712	H	3.449504	3.689658	0.936659

H	-3.183150	-0.982645	-0.432862	H	-3.065911	-1.023288	-4.616148	H	1.777847	3.088395	0.799434
H	-4.414185	-1.437222	-1.640258	H	-3.211489	-0.255515	-3.013960	H	2.759342	3.262430	-0.650282
C	-3.377876	1.152842	-2.748366	C	-1.324059	-2.663234	-2.821018	H	-1.008225	1.483515	2.592991
H	-2.979688	1.761919	-3.563332	H	-1.853648	-3.238122	-3.587196	H	0.459815	2.039365	1.984423
H	-4.446531	0.973316	-2.904390	H	-0.408643	-3.186352	-2.536779	H	-1.775768	3.096421	-0.785767
H	-3.234887	1.694545	-1.809784	H	-1.963707	-2.577468	-1.938567	H	-2.756287	3.261322	0.665670
C	-3.329142	-1.047280	2.887768	C	-2.934933	1.092862	-0.288163	H	-3.446656	3.700917	-0.917828
H	-2.924838	-1.675116	3.685297	H	-2.251556	1.009380	-1.138185	H	-2.705187	1.093004	-2.889724
H	-4.380724	-0.818941	3.089428	H	-3.293302	0.095667	-0.024449	H	-4.293186	1.904203	-2.779752
H	-3.252121	-1.594042	1.944370	H	-3.780511	1.730978	-0.563916	H	-4.159416	0.131312	-2.568771
C	-3.232689	1.514484	1.559890	C	-3.327488	2.121242	2.375185	H	-5.090190	1.694091	1.155640
H	-2.797925	2.516127	1.523427	H	-2.898035	2.664303	3.219694	H	-5.680065	0.534153	-0.047149
H	-3.141520	1.076099	0.564822	H	-4.150608	2.697378	1.939732	H	-5.650693	2.286633	-0.432676
H	-4.291797	1.590851	1.826008	H	-3.708689	1.161919	2.735178	H	-1.165695	-4.466404	2.351897
C	-2.736495	1.366642	4.369404	C	-1.648590	3.516840	0.473638	H	-0.730477	-4.010348	0.689063
H	-3.821019	1.476705	4.473596	H	-1.055760	3.434691	-0.440481	H	-2.439907	-4.108447	1.139881
H	-2.333325	0.795448	5.207829	H	-2.585784	4.031681	0.238559	H	-2.178412	-2.805175	4.202299
H	-2.270651	2.355553	4.366736	H	-1.093614	4.083919	1.223426	H	-3.539859	-2.285767	3.163515
H	-0.008579	2.807471	0.590210	H	2.231937	-2.125644	-1.479707	H	-2.504631	-1.070951	3.939012
H	-0.047735	2.132157	-0.971765	H	1.656512	-2.752871	-0.022921	H	1.005153	-1.891205	1.894105
H	-0.084476	-2.177952	0.973179	H	-1.529888	-2.693935	0.253433	H	0.465053	-2.659881	3.413457
H	-0.123744	-2.853308	-0.588775	H	-2.088219	-1.923313	1.646762	H	0.332253	-0.893156	3.186459

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