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Supporting Information

Ambiguous reactivity of Li/Cl phosphinidenoid complexes under redox conditions – a novel dichotomy in phosphorus chemistry

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1. Preparative methods

All reactions and manipulations were carried out under an atmosphere of dry argon, using Schlenk and vacuum line techniques. Argon was cleaned over a BTS catalyst; the drying of the Ar gas occured via silica gel and P_2O_5. Solvents were dried according to standard procedures[1] and stored in brown glasses over sodium wire, and under inert gas atmosphere.

Analytical methods

Mass spectrometry: Electron ionization (70eV) mass spectra were recorded on a Kratos MS 50 or on a MAT 95XL Finnigan spectrometer.

NMR spectra were recorded on a Bruker AX 300 spectrometer (^{1}H: 300.1 MHz, ^{13}C: 75.0 MHz and ^{31}P: 121.5 MHz,) using $CDCl_3$ as solvent; shifts are given relative to external tetramethylsilane (^{1}H, ^{13}C,) and 85% H_3PO_4 (^{31}P).

Single-crystal structure analysis: Crystal structures were recorded on a Bruker X8-KappaApex-II diffractometer and a Bruker D8-Venture diffractometer. The structures were solved by intrinsic phasing (SHELXT) and refined by full-matrix least squares on F2 (SHELXL). All non-hydrogens were refined anisotropically. Hydrogen atoms were included isotropically using the riding model on the bound atoms. Absorption corrections were carried out semi-empirically from equivalents. Additionally, some calculation of bond lengths and angles were obtained using the Ortep32 program.

Synthesis of complex 3

500 mg (0.75 mmol) of $[W(CO)_5(CPh_3PCl_2)]$ were dissolved in THF (10 mL) and 120 µL (1eq.) of 12-crown-4 were added. The solution was then cooled to -100 °C and 1.2 eq. of ^{t}BuLi (1.7 M in *n*-pentane) were added dropwise. Afterwards hexafluoroacetone was bubbled through the solution for a few seconds until the color changed from yellowish to deep green. Subsequently, the solvent was removed in *vacuo* (*ca.* 0.01 bar) at low temperature (-20 °C) and the residue extracted with 45 mL of *n*-pentane. The product was purified by washing with *n*-pentane at -30 °C.

3: Light yellow solid. Yield: 460 mg (0.50 mmol, 92 %); m.p. 110 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ = 7.1−7.5 (m, 15H, 3Ph); ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 73.9 (d, $^1J_{C,P}$ = 9.1 Hz, P-$\underline{C}$Ph$_3$), 107.5 (br m, $CF_3\underline{C}CF_2$), 119.3 (q m, $^1J_{C,F}$ = 274 Hz, CF_3), 125.9 (s, *p*-Ph), 127.3 (d, $^4J_{C,P}$ = 1.5 Hz, *m*-Ph), 127.7 (d, $^4J_{C,P}$ = 1.6 Hz, *m*-Ph), 127.8 (d, $^3J_{C,P}$ = 3.1 Hz, *o*-Ph), 127.9 (s, *p*-Ph), 128.1 (d, $^4J_{C,P}$ = 1.2 Hz, *m*-Ph), 128.3 (d, $^3J_{C,P}$ = 3.2 Hz, *o*-Ph), 128.5 (d, $^4J_{C,P}$ = 1.8 Hz, *m*-Ph), 129.1 (s, *p*-Ph), 130.6 (d, $^3J_{C,P}$ = 7.7 Hz, *o*-Ph), 131.1 (d, $^3J_{C,P}$ = 8.3 Hz, *o*-Ph), 138.4 (d, $^2J_{C,P}$ = 4.5 Hz, *ipso*-Ph), 139.9 (d, $^2J_{C,P}$ = 7.1 Hz, *ipso*-Ph), 140.4 (d, $^2J_{C,P}$ = 13.6 Hz, *ipso*-Ph), 155.7 (pt m, $^1J_{C,F}$ = 297 Hz, CF_2), 194.0 (ddsat, $^2J_{C,P}$ = 7.1 Hz, $J_{C,F}$ < 1 Hz, $J_{C,W}$ = 127.5 Hz, *cis*-CO), 195.7 (d, $^2J_{C,P}$ = 45.4 Hz, *trans*-CO); ^{19}F{^{1}H} NMR ($CDCl_3$): -63.2 (d m, 3F, $J_{F,F}$ = 23 Hz CF_3), -77.2 (d m, 1F, $J_{F,F}$ = 23 Hz, C=CF), -92.5 (pquint

m, 1F, $J_{F,F}$ = 23 Hz, C=CF); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): 200.6 (t_{sat}, $^{1}J_{W,P}$ = 336.5 Hz; "$J_{P,F}$ = 6.0 Hz"). IR (neat): ṽ [cm^{-1}] = 2084, 2017, 2003, 1958, 1941, (s, CO). MS (EI, ^{184}W): m/z (%): 780 $[M]^+$, 640.0 (30) $[M\text{-}5CO]^+$; 455.9 (20) $[M\text{-}5CO\text{-}W]^+$; 309.1 (30) $[M\text{-}5CO\text{-}W\text{-}C_3F_5O]^+$; 243.1 (100) $[CPh_3]^+$. Elemental analysis (%) calculated for $C_{27}H_{15}ClF_5O_6PW$ (%) C: 41.54, H: 1.94; found: C: 41.27, H: 2.26.

Synthesis of complex 4

500 mg (0.89 mmol) of $[W(CO)_5(Cp^*PCl_2)]$ were dissolved in THF (10 mL) and 176 µL (1eq.) of 12-crown-4 were added. The solution was then cooled to -100 °C and 1.2 eq. of ^{t}BuLi (1.7 M in *n*-pentane) were added dropwise. Afterwards, hexafluoroacetone was bubbled through the solution for a few seconds until the color changed from dark yellow to green. Subsequently, the solvent was removed in *vacuo* (*ca.* 0.01 bar) at low temperature (-20 °C) and the residue extracted with 45 mL of *n*-pentane. The product was purified by washing with *n*-pentane at -30 °C.

4: Light yellow solid. Yield: 460 mg (0.53 mmol, 91 %); m.p. 126 °C; ^{1}H NMR ($CDCl_3$) δ = 1.43 (d, 3H, $^{3}J_{P,H}$ = 14.1 Hz, Cp*-C^{1}-CH_3), 1.77 (d, 6H, $J_{P,H}$ = 3.2 Hz, Cp*-CH_3), 1.87 (d, 6H, $J_{P,H}$ = 15.4 Hz Cp*-CH_3); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 11.6 (d, $J_{C,P}$ = 3.7 Hz, Cp*-CH_3), 11.9 (d, $J_{C,P}$ = 1.9 Hz, Cp*-CH_3), 12.7 (br s, Cp*-CH_3), 13.6 (d, $J_{C,P}$ = 7.2 Hz, Cp*-CH_3), 69.2 (d, $^{1}J_{C,P}$ = 6.3 Hz, P-Cp*), 106.9 (br m, $CF_3\underline{C}CF_2$), 121.6 (qdd, $^{1}J_{C,F}$ = 269.7, CF_3), 135.2 (d, $J_{C,P}$ = 8.9 Hz, Cp*-ring-C), 135.6 ($J_{C,P}$ = 5.9 Hz, Cp*), 145.3 (d, $J_{C,P}$ = 9.1 Hz, Cp*-ring-C), 145.5 (d, $J_{C,P}$ = 9.1 Hz, Cp*-ring-C), 155.9 (ddq, $^{1}J_{C,F}$ = 298.8 Hz, CF_2), 194.5 (ddsat, $^{2}J_{C,P}$ = 7.6, $J_{C,F}$ = 1.9 Hz, $J_{C,W}$ = 128.3 Hz, *cis*-CO), 195.7 (d, $^{2}J_{C,P}$ = 42.9 Hz, *trans*-CO); $^{19}F\{^{1}H\}$ NMR ($CDCl_3$): -65.3 (dd, 3F, $J_{F,F}$ = 20.6 Hz, CF_3), -76.6 (dq, 1F, $J_{F,F}$ = 52.3 Hz, C=CF), -88.9 (dq, 1F, $J_{F,F}$ = 59.2 Hz, C=CF); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): 193.2 ppm ($t_{sat,}$ $^{1}J_{W,P}$ = 344.4 Hz, $^{4}J_{P,F}$ = 7.2 Hz). IR (neat): ṽ [cm^{-1}] = 2077 s, 1998 br, 1919 s (CO). MS (EI, ^{184}W): m/z (%): 672 (100) $[M]^+$, 616.0 (30) $[M\text{-}2CO]^+$; 588.0 (70) $[M\text{-}2CO\text{-}CO]^+$; 532.0 (90) $[M\text{-}2CO\text{-}CO\text{-}2CO]^+$; 348.1 (10) $[M\text{-}2CO\text{-}CO\text{-}2CO\text{-}W]^+$; 201.1 (10) $[M\text{-}2CO\text{-}CO\text{-}2CO\text{-}W\text{-}C_3F_5O]^+$. Elemental analysis (%) calculated for $C_{18}H_{15}ClF_5O_6PW$ (%) C: 32.15, H: 2.25; found: C: 32.41, H: 2.83.

Synthesis of complex 5

500 mg (0.85 mmol) of $[W(CO)_5\{(Me_3Si)_2HCPCl_2\}]$ were dissolved in THF (10 mL) and 138 µL (1eq.) of 12-crown-4 were added. The solution was then cooled to -100 °C and 1.2 eq. of ^{t}BuLi [1.7 M in *n*-pentane] were given dropwise. Afterwards, hexafluoroacetone was bubbled through the solution for a few seconds until the color changed from dark yellow to a light green. Subsequently, the solvent was removed in *vacuo* (*ca.* 0.01 bar) at low temperature (-20 °C) and the residue extracted with 45 mL of *n*-pentane. In addition to the main product **5,** two phosphorus resonances with lower intensity were observed at 31.0 ppm (~20%, m_c) and 176.8 ppm (~10%, m_c). A separation of the product mixture was not possible, neither by recrystallisation nor by chromatography. Therefore, complex **5** could only be characterized from this solution by means of multinuclear NMR spectroscopy, but its molecular structure was confirmed by X-ray crystallography.

5: ^{1}H NMR ($CDCl_3$) δ = 0.21 (s, 9H, $Si(CH_3)_3$), 3.3 (d, $^{2}J_{P,H}$ = 9.5 Hz, 2H, PCH2), 9.6 (d, $^{2}J_{P,H}$ = 36.5 Hz, 1H, P-OH), (PC-OH, not found); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 1.66 (d, $^{3}J_{C,P}$ = 6.6 Hz, $Si(CH_3)_3$), 49.3 (d, $^{1}J_{C,P}$ = 117.0 Hz, CH_2P), 122.4 (q m, $^{1}J_{C,F}$ = 287 Hz, CF_3), 123.7 (q m, $^{1}J_{C,F}$ = 285 Hz, CF_3), ($F_3C\underline{C}CF_3$, not found), 194.3 (d, $^{2}J_{C,P}$ = 9.3 Hz, *cis*-CO), 196.6 (d, $^{2}J_{C,P}$ = 35.2 Hz, *trans*-CO);

$^{19}F\{^{1}H\}$ NMR ($CDCl_3$): -67.1 (m_c, 3F, CF_3,), -67.5 (m_c, 3F, CF_3); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): 247.6 (m_{sat} , $^{1}J_{W,P}$ = 277.8 Hz, $^{2}J_{P,H}$ = 36.5 Hz).

Crystal structure data of complex 3

Summary of Data CCDC 1516181; Empirical formula: $C_{27}H_{15}ClF_5O_6PW$; Formula weight: 780.66; Temperature/K: 100; Crystal system: monoclinic; Space group: $P2_1/c$; a/Å: 15.3052(7); b/Å: 9.5908(4); c/Å: 37.3062(16); α/°: 90; β/°: 101.829(2); γ/°: 90; Volume/Å: 5359.9(4); Z: 8; ρ_{calc}g/mm^3: 1.935; μ/mm^{-1}: 4.576; F(000): 3008.0; Crystal size/mm^3: 0.07 × 0.05 × 0.02; 2Θ range for data collection: 3144 to 51.998°; Index ranges: $-9 \leq h \leq 18$, $-7 \leq k \leq 11$, $-46 \leq l \leq 43$; Reflections collected: 48898; Independent reflections: 10691; [R_{int} = 0.0373, R_{sigma} = 0.0343]; Data/restraints/parameters: 10691/48/743; Goodness-of-fit on F^2: 1.106; Final R indexes [I>=2σ (I)]: R_1 = 0.0258, wR_2 = 0.0566; Final R indexes [all data]: R_1 = 0.0272, wR_2 = 0.0572; Largest diff. peak/hole / e Å^{-3}: 1.83/-0.97.

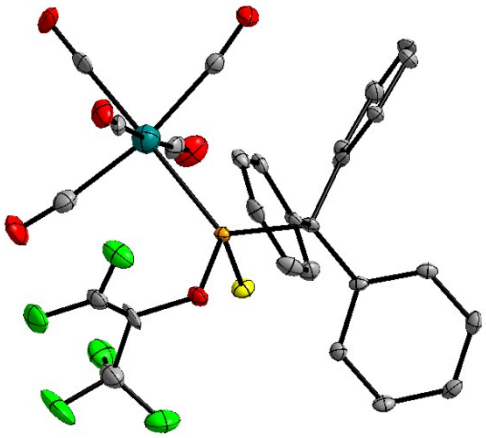

Figure S1. Molecular structure of complex **3**. Diamond 3.0 (ellipsoids 50% probability). Hydrogen atoms were removed for clarity.

Crystal structure data of complex 4

Summary of Data CCDC 1516182; Empirical formula: $C_{18}H_{15}ClF_5O_6PW$; Moiety formula: $C_{18}H_{15}ClF_5O_6PW$; Formula weight: 672.57; Temperature/K: 100; Crystal system: monoclinic; Space group: C2/c; a/Å: 18.4900(10); b/Å: 14.6863(8); c/Å: 17.1298(10); α/°: 90; β/°: 107.5984(15); γ/°: 90; Volume/Å: 4433.9(4); Z: 8; ρ_{calc}g/mm^3: 2.015; μ/mm^{-1}: 5.477; F(000): 2576.0; Crystal size/mm^3: 0.25 × 0.24 × 0.12; 2Θ range for data collection: 6.084 to 55.994°; Index ranges: $-21 \leq h \leq 24$, $-18 \leq k \leq 19$, $-22 \leq l \leq 22$; Reflections collected: 17104; Independent reflections: 5353; [R_{int} = 0.0314, R_{sigma} = 0.0287]; Data/restraints/parameters: 5353/0/294; Goodness-of-fit on F^2: 1.031; Final R indexes [I>=2σ (I)]: R_1 = 0.0206, wR_2 = 0.0521; Final R indexes [all data]: R_1 = 0.0225, wR_2 = 0.0530; Largest diff. peak/hole / e Å^{-3}: 1.93/-1.12.

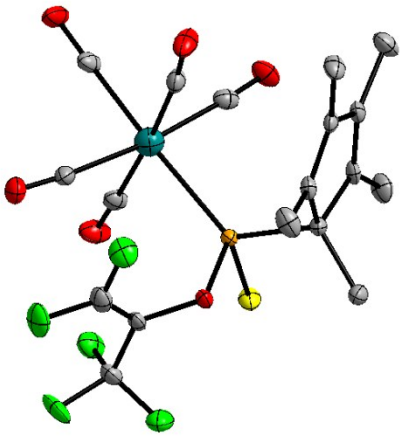

Figure S2. Molecular structure of complex **4**. Diamond 3.0 (ellipsoids 50% probability). Hydrogen atoms were removed for clarity.

Crystal structure data of complex 5

Summary of Data CCDC 1516183; Empirical formula: $C_{12}H_{13}F_6O_7PSiW$; Moiety formula: $C_{12}H_{13}F_6O_7PSiW$; Formula weight: 626.13; Temperature/K: 100; Crystal system: monoclinic; Space group: C2/c; a/Å: 18.3148(17); b/Å: 9.0555(8); c/Å: 24.691(2); α/°: 90; β/°: 100.327(3); γ/°: 90; Volume/Å: 4028.7(6); Z: 8; ρ_{calc}g/mm^3: 2.065; μ/mm^{-1}: 5.958; F(000): 2384.0; Crystal size/mm^3: 0.24 × 0.18 × 0.16; 2Θ range for data collection: 5.034 to 55.998°; Index ranges: $-24 \leq h \leq 24$, $-11 \leq k \leq 11$, $-31 \leq l \leq 32$; Reflections collected: 52053; Independent reflections: 4867; [R_{int} = 0.0692, R_{sigma} = 0.0327]; Data/restraints/parameters: 4867/18/258; Goodness-of-fit on F^2: 1.176; Final R indexes [I>=2σ (I)]: R_1 = 0.0353, wR_2 = 0.0774; Final R indexes [all data]: R_1 = 0.0384, wR_2 = 0.0786; Largest diff. peak/hole / e Å^{-3}: 2.41/-2.07.

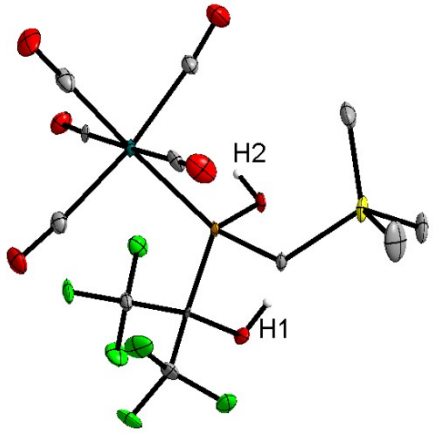

Figure S3. Molecular structure of complex **5**. Diamond 3.0 (ellipsoids 50% probability). Hydrogen atoms, except for H1 and H2, were removed for clarity.

3. Computational methods

The energies of all complexes included in this study were computed at the BP86-D3/def2-TZVP level of theory. The calculations have been performed by using the program TURBOMOLE version 7.0. [2] For the calculations we have used the BP86 functional with the latest available correction for dispersion (D3).[3] In order to reproduce solvent effects, we have used the conductor-like screening model COSMO, which is a variant of the dielectric continuum solvation models.[4] We have used THF as solvent. The nature of stationary points has been confirmed by performing frequency calculations at the same level. Both the open singlet and the triplet states of the solvent cage radical pair given in Figure 4 have been computed at the UBP86-D3/def2-TZVP level of theory do not present spin contamination; the $<S^2>$ values are 0.0 and 2.005425, for the singlet and triplet, respectively. We have only used the open singlet in the mechanism depicted in Figure 4 of the main text because it is lower in energy and the spin of the electrons is adequate for the subsequent formation of the P–O sigma bond.

Additional Figures

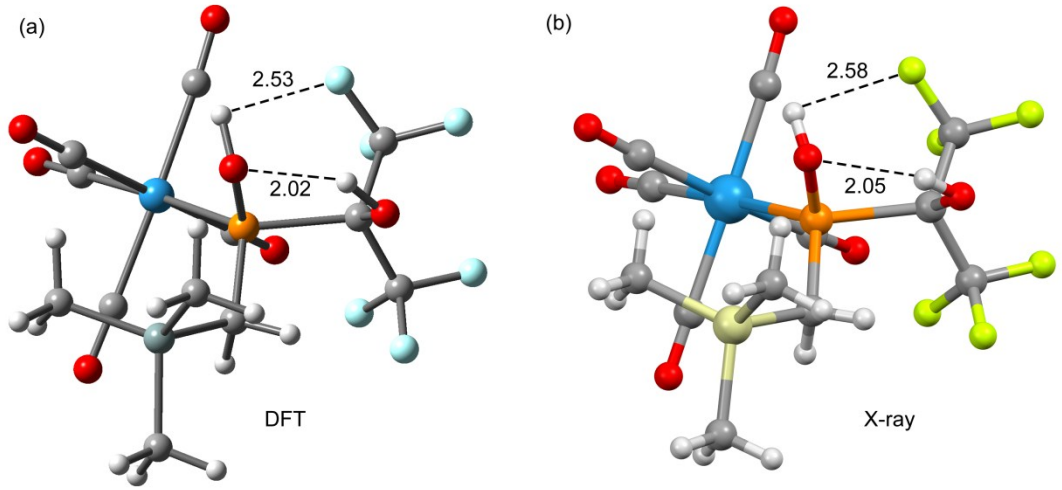

Figure S4. DFT and X-ray structure of compound **5** with indication of the intramolecular H-bonds.

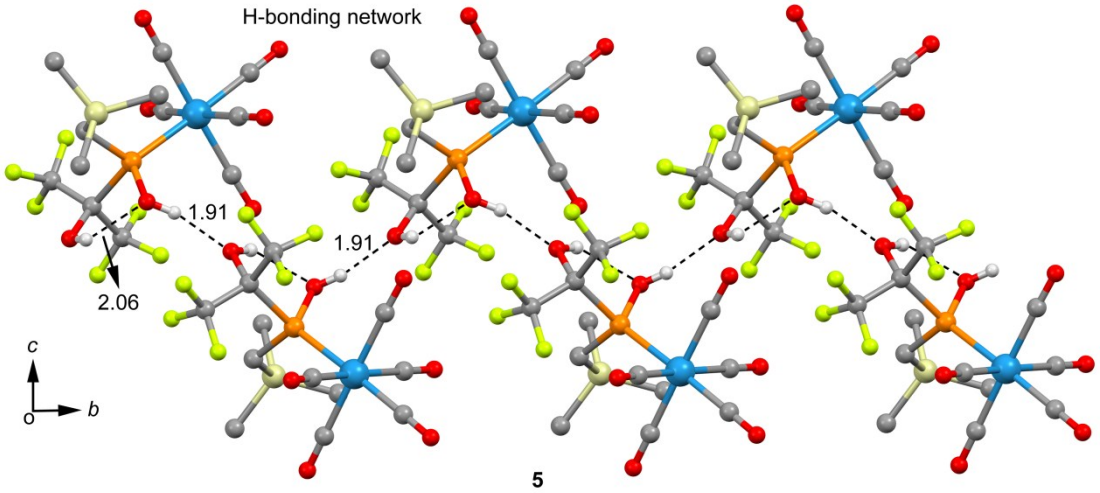

Figure S5. H-bonding network observed in the solid state X-ray structure of **5**. H-atoms omitted for clarity.

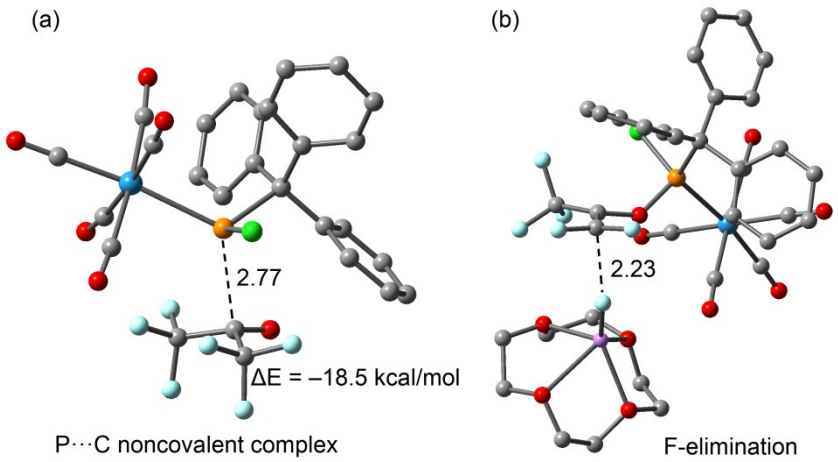

Figure S6. (a) noncovalent π-hole complex between the phosphinidenoid anion and perfluoroacetone and its binding energy. (b) Resulting product of the E_1cB_I elimination promoted by Li^+@12-c-4.

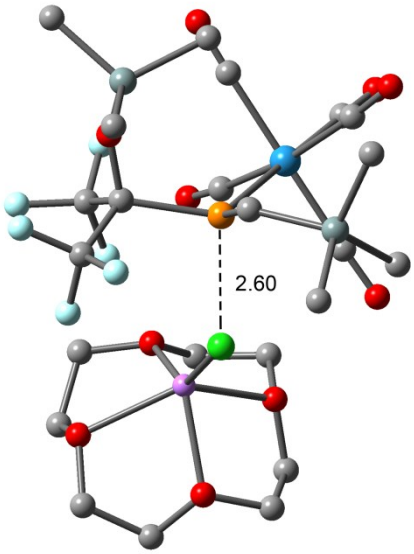

Figure S7. Resulting product of the Cl elimination promoted by Li^+@12-c-4. Distance in Å. H-atoms omitted for clarity.

4. Cartesian Coordinates (Figure 4)

Reactants

P	-0.1793296	-1.6533347	0.9999073
W	-2.5686022	-2.2425076	0.0730997
C	-3.1954388	-0.3337781	-0.3375945
C	-3.2433872	-1.9401505	1.9783548
C	-4.3625189	-2.8823284	-0.5560255
C	-1.7129221	-2.5369352	-1.7847849
C	-2.0918461	-4.1796456	0.5740849

O	-3.6448810	0.7216141	-0.5367260
O	-5.3983853	-3.2656208	-0.9445253
O	-1.2350599	-2.7620511	-2.8148894
O	-1.8763591	-5.2825998	0.8683401
O	-3.6078240	-1.7521039	3.0695216
Cl	1.1872873	-3.0606152	0.1499117
C	0.5691250	0.0029508	0.2336228
C	0.4855044	-0.0345330	-1.2857818
C	-0.5718141	0.5719985	-1.9883047
C	1.4484854	-0.7278579	-2.0463289
C	-0.6655264	0.4934944	-3.3776492
H	-1.3353285	1.1181299	-1.4409082
C	1.3558606	-0.8069099	-3.4360667
H	2.2803060	-1.2118736	-1.5399298
C	0.3002506	-0.1951350	-4.1148897
H	-1.5087419	0.9691119	-3.8821746
H	2.1142190	-1.3636555	-3.9901044
H	0.2234181	-0.2664199	-5.2012048
C	-0.2342010	1.1687943	0.8466292
C	-1.1331435	0.9938509	1.9062445
C	-0.0289795	2.4762949	0.3735522
C	-1.8306736	2.0745748	2.4529406
H	-1.2932406	-0.0036690	2.3193752
C	-0.7172762	3.5599963	0.9170615
H	0.6750131	2.6412131	-0.4429538
C	-1.6301260	3.3634154	1.9585998
H	-2.5394810	1.8969002	3.2631782
H	-0.5416987	4.5630835	0.5230900
H	-2.1776520	4.2087439	2.3795639
C	2.0130717	0.2017918	0.7495968
C	2.9546053	0.9352745	0.0074363
C	2.3927125	-0.2407943	2.0257011
C	4.2308456	1.1960638	0.5113179
H	2.6877893	1.3020632	-0.9834820
C	3.6677051	0.0146172	2.5319369
H	1.6659510	-0.8061053	2.6129308
C	4.5987513	0.7324173	1.7766373
H	4.9406896	1.7656230	-0.0924525
H	3.9347136	-0.3533043	3.5248170

H	5.5981324	0.9299114	2.1693245

C	0.00000000	1.38319450	-0.12204044
C	-0.00000000	-0.00000000	0.63396621
C	-0.00000000	-1.38319450	-0.12204044
O	-0.00000000	-0.00000000	1.83433341
F	-1.09757498	2.07120876	0.25936249
F	0.00000000	1.29516430	-1.46394605
F	1.09757498	2.07120876	0.25936249
F	-1.09757498	-2.07120876	0.25936249
F	1.09757498	-2.07120876	0.25936249
F	-0.00000000	-1.29516430	-1.46394605

Solvent cage radical pair

C	0.8353767	-2.2751893	-3.5620853
C	0.7520901	-0.7929845	-3.4574839
F	1.9850212	-2.8065486	-2.9727945
F	0.8424933	-2.7228499	-4.8496355
F	-0.1934650	-2.9082917	-2.9154216
C	1.1513760	0.0312257	-4.6461369
F	1.2095940	1.3479238	-4.3315304
F	2.3922146	-0.3056965	-5.1680020
F	0.2881513	-0.0808579	-5.7177768
O	0.5963025	-0.2141946	-2.3052289
P	-0.7188481	-1.0042588	-0.3895624
Cl	-0.7685535	-2.9444013	0.4606656
C	0.3725151	-0.0154945	0.9187026
W	-3.0585933	-0.2380670	-1.0288119
C	-4.9263551	0.2300115	-1.6072886
C	-2.2588067	0.9329913	-2.5412559
C	-3.1652673	-1.8884929	-2.2684952
C	-3.1553562	1.4387007	0.1557027
C	-3.7923837	-1.3543709	0.5303458
O	-1.8663695	1.6303517	-3.3745597
O	-3.3128480	-2.7958336	-2.9706070
O	-6.0185694	0.4923639	-1.9234970
O	-3.3318493	2.3836916	0.8045092
O	-4.2122339	-1.9657322	1.4220511
C	-0.0037421	-0.5924735	2.2833539

C	0.9097128	-1.3228310	3.0553550
C	-1.3168696	-0.4531709	2.7714062
C	0.5265659	-1.8916721	4.2737598
H	1.9277037	-1.4602856	2.6935989
C	-1.7025821	-1.0246385	3.9798262
H	-2.0473677	0.0973161	2.1804161
C	-0.7794155	-1.7483838	4.7428225
H	1.2574465	-2.4596878	4.8525058
H	-2.7337309	-0.9151307	4.3186526
H	-1.0808829	-2.2024045	5.6884136
C	0.0206045	1.4752240	0.7902089
C	0.0626798	2.1020775	-0.4681129
C	-0.2446197	2.2716923	1.9153012
C	-0.2059337	3.4637915	-0.5979349
H	0.3163816	1.5175092	-1.3539225
C	-0.4967480	3.6395380	1.7853546
H	-0.2513030	1.8232915	2.9073980
C	-0.4932643	4.2412862	0.5268566
H	-0.1905783	3.9129777	-1.5922671
H	-0.7091495	4.2316734	2.6773034
H	-0.7105085	5.3058510	0.4230920
C	1.8683224	-0.2027464	0.6112147
C	2.7871941	0.7316823	1.1151959
C	2.3644991	-1.2955213	-0.1094929
C	4.1586128	0.5777827	0.9046791
H	2.4214222	1.5938777	1.6736953
C	3.7343813	-1.4474980	-0.3312090
H	1.6809352	-2.0313737	-0.5276142
C	4.6394760	-0.5130552	0.1755596
H	4.8515305	1.3215497	1.3028784
H	4.0838037	-2.2938013	-0.9236974
H	5.7097880	-0.6264421	-0.0064010

I

C	0.8596528	-1.2034674	-2.7740258
O	-0.1860812	-0.3771142	-2.2401973
P	-0.9365824	-0.4294213	-0.8044064
Cl	-1.4721957	-2.4294579	-0.5304125
C	0.3098193	-0.1378829	0.7162764

W	-3.0140951	1.0237408	-1.1555730
C	-4.6621518	2.0602104	-1.6583399
C	-3.4419472	-0.2793405	-2.7041872
C	-4.1026486	-0.1459493	0.1362759
C	-1.8682040	2.1840467	-2.4214638
C	-2.7188806	2.4072745	0.3308800
O	-3.7465212	-0.9706952	-3.5779313
O	-4.7325203	-0.7906629	0.8661044
O	-5.6177140	2.6545051	-1.9622537
O	-1.2397228	2.8601166	-3.1182834
O	-2.6415540	3.2257783	1.1497478
C	1.9936611	-0.4208969	-3.2225874
C	0.3923027	-2.3587046	-3.5369923
F	-0.9568503	-2.3307254	-3.8071820
F	0.5640785	-3.6092561	-2.8913118
F	1.0427674	-2.5456263	-4.7348933
F	1.8047771	0.4120416	-4.3642102
F	2.4165822	0.4885192	-2.2706868
F	3.0718884	-1.1922591	-3.5571268
C	0.3763531	1.3885020	0.8464867
C	0.3095312	2.0286802	2.0926282
C	0.6064004	2.1799062	-0.2922077
C	0.4384238	3.4155230	2.1943168
H	0.1614584	1.4372012	2.9950116
C	0.7161032	3.5658169	-0.1943876
H	0.7269178	1.7067125	-1.2653760
C	0.6284695	4.1928680	1.0507032
H	0.3762938	3.8894183	3.1755728
H	0.8704657	4.1513814	-1.1013848
H	0.7086107	5.2782879	1.1288654
C	-0.3677234	-0.8045348	1.9153445
C	0.1948161	-1.9149528	2.5625021
C	-1.6183480	-0.3454841	2.3713954
C	-0.4751353	-2.5527275	3.6099344
H	1.1646438	-2.2888723	2.2396181
C	-2.2949166	-0.9885454	3.4050014
H	-2.0699728	0.5271311	1.9046862
C	-1.7270690	-2.1019293	4.0314963
H	-0.0124458	-3.4155899	4.0925405

H	-3.2742177	-0.6201553	3.7135297
H	-2.2557064	-2.6104345	4.8395391
C	1.7209034	-0.6993661	0.4587754
C	1.9349818	-1.9571710	-0.1295505
C	2.8426375	0.0309431	0.8771081
C	3.2274476	-2.4577084	-0.2965853
H	1.0979592	-2.5642267	-0.4586445
C	4.1368087	-0.4682931	0.7088691
H	2.7112590	1.0133638	1.3287090
C	4.3346254	-1.7159687	0.1161262
H	3.3589118	-3.4228775	-0.7866514
H	4.9894577	0.1313066	1.0325668
H	5.3441952	-2.1029777	-0.0337589

Final products

W	0.3771751	1.4587286	-2.7663332
Cl	-2.6404176	-0.2395892	-1.1903676
P	-0.5669650	-0.1181751	-1.0368477
F	-1.7930802	-3.8175056	-1.8996048
F	-0.7609636	-4.0571146	-3.8208726
F	-1.9818870	-2.2850538	-3.4416230
F	2.3828025	-2.1827508	-1.9548375
F	1.7628853	-3.4095023	-3.6470001
O	-0.1651423	-1.7436101	-1.1201457
O	1.3043748	3.4006058	-5.1113113
O	-2.4303198	3.0317442	-2.7292095
O	1.5738382	3.6920573	-0.7876696
O	3.3920982	0.3547329	-2.7998828
O	-0.4641428	-0.4781905	-5.1918944
C	0.0849373	-2.4601920	-2.2658607
C	-1.1093776	-3.1569277	-2.8771811
C	1.3624204	-2.6801308	-2.6250000
C	-0.2785472	0.0544858	0.8923021
C	-0.2715131	1.5626629	1.1887301
C	-1.2752745	2.4040076	0.6789663
H	-2.0593621	1.9980179	0.0422461
C	-1.3095728	3.7611868	0.9966982
H	-2.0908496	4.3909544	0.5698678
C	-0.3518845	4.3053234	1.8542586

H	-0.3732423	5.3671622	2.1013865
C	0.6305817	3.4748440	2.3954716
H	1.3776128	3.8821335	3.0778178
C	0.6713818	2.1188959	2.0645876
H	1.4424630	1.4860479	2.5007289
C	-1.3813493	-0.6430870	1.7086876
C	-1.9753673	0.0174073	2.7955325
H	-1.6781051	1.0348151	3.0421604
C	-2.9475755	-0.6095501	3.5798418
H	-3.3870284	-0.0683720	4.4188825
C	-3.3552079	-1.9115596	3.2925679
H	-4.1177700	-2.3997792	3.9006351
C	-2.7741981	-2.5824606	2.2137437
H	-3.0813038	-3.6000706	1.9689559
C	-1.7994871	-1.9596939	1.4358100
H	-1.3651044	-2.5082742	0.6039965
C	1.1110487	-0.5785979	1.0840871
C	1.3057178	-1.7601461	1.8123549
H	0.4632417	-2.2379570	2.3080106
C	2.5754603	-2.3329312	1.9216412
H	2.6989078	-3.2501099	2.4992003
C	3.6771478	-1.7418023	1.3010281
H	4.6655880	-2.1955779	1.3816084
C	3.5011954	-0.5550656	0.5861107
H	4.3479067	-0.0732669	0.0964272
C	2.2360805	0.0200608	0.4877201
H	2.1240913	0.9601236	-0.0479267
C	0.9750908	2.7009880	-4.2493830
C	-1.4407544	2.4365100	-2.7480184
C	1.0988504	2.8662485	-1.4411513
C	2.2828426	0.6822501	-2.7738876
C	-0.1999479	0.1750502	-4.2760553

O	1.34638660	-1.43768730	-0.58640160
O	1.43768730	1.34638660	-0.58640160
O	-1.34638660	1.43768730	-0.58640160
O	-1.43768730	-1.34638660	-0.58640160
C	2.07876210	-0.77100020	0.43941270
C	2.54451320	0.55241260	-0.14921900

C	0.77100020	2.07876210	0.43941270
C	-0.55241260	2.54451320	-0.14921900
C	-2.07876210	0.77100020	0.43941270
C	-2.54451320	-0.55241260	-0.14921900
C	-0.77100020	-2.07876210	0.43941270
C	0.55241260	-2.54451320	-0.14921900
Li	0.00000000	0.00000000	-1.82004360
H	1.44999290	-0.59750180	1.33380610
H	2.95067270	-1.37609380	0.75532120
H	3.13966010	0.36088280	-1.05290080
H	3.16939460	1.09922170	0.58006740
H	0.59750180	1.44999290	1.33380610
H	1.37609380	2.95067270	0.75532120
H	-0.36088280	3.13966010	-1.05290080
H	-1.09922170	3.16939460	0.58006740
H	-1.44999290	0.59750180	1.33380610
H	-2.95067270	1.37609380	0.75532120
H	-3.13966010	-0.36088280	-1.05290080
H	-3.16939460	-1.09922170	0.58006740
H	-0.59750180	-1.44999290	1.33380610
H	-1.37609380	-2.95067270	0.75532120
H	0.36088280	-3.13966010	-1.05290080
H	1.09922170	-3.16939460	0.58006740
F	0.00000000	0.00000000	-3.46030020

Cartesian Coordinates (Figure 5)

Reactants

C	0.00000000	1.38319450	-0.12204044
C	-0.00000000	-0.00000000	0.63396621
C	-0.00000000	-1.38319450	-0.12204044
O	-0.00000000	-0.00000000	1.83433341
F	-1.09757498	2.07120876	0.25936249
F	0.00000000	1.29516430	-1.46394605

F	1.09757498	2.07120876	0.25936249
F	-1.09757498	-2.07120876	0.25936249
F	1.09757498	-2.07120876	0.25936249
F	-0.00000000	-1.29516430	-1.46394605

I1

C	2.5883667	0.4662364	-0.4704882
O	2.1179120	1.5352514	0.1289352
C	3.9543338	-0.0560586	0.1624500
C	2.8929099	0.6206977	-2.0284194
F	3.9882160	0.1846333	1.4923915
F	5.0369506	0.5965116	-0.3576282
F	4.1773426	-1.3887046	-0.0180767
F	3.6657370	-0.3794924	-2.5365473
F	3.5408292	1.7925899	-2.2650267
F	1.7716497	0.6555556	-2.8041736
P	1.1110433	-0.7381617	-0.0804542
Cl	1.3390821	-2.4581342	-1.3629470
C	-0.3547321	0.0638629	-0.8711803
H	-0.1115584	0.0311501	-1.9457733
Si	-0.6346587	1.9682386	-0.5939837
Si	-1.9799350	-0.9927425	-0.8723768
C	-0.6190708	2.4829563	1.2108386
H	0.4110682	2.5615854	1.5728992
H	-1.1586051	1.7623213	1.8412062
H	-1.1170384	3.4597596	1.3155677
C	-2.3798861	2.4192195	-1.2497029
H	-3.1832344	2.2675297	-0.5206948
H	-2.6560497	1.8954117	-2.1764032
H	-2.3488339	3.4942532	-1.4879271
C	0.4066773	3.0983182	-1.6903217
H	1.4691123	3.0682976	-1.4375522
H	0.0297707	4.1250262	-1.5500910
H	0.2753973	2.8404340	-2.7514159
C	-3.4554110	-0.2537594	0.0659311
H	-3.1642820	0.4220149	0.8774835
H	-4.0195656	-1.0811946	0.5209593
H	-4.1270709	0.2891051	-0.6117226
C	-2.4243159	-1.1187202	-2.7081846

H	-3.3846883	-1.6408742	-2.8371379
H	-1.6475570	-1.6911617	-3.2374699
H	-2.5030193	-0.1323843	-3.1871010
C	-1.9052104	-2.7640072	-0.2328074
H	-1.8878146	-2.7963505	0.8632695
H	-1.0644687	-3.3525508	-0.6123632
H	-2.8436763	-3.2424637	-0.5595498
W	0.9334325	-1.4519282	2.4161614
C	0.7917193	-1.9605512	4.3482514
C	1.5593026	0.4405861	2.9887423
C	2.8588803	-2.1879650	2.5322652
C	0.4497922	-3.3744222	1.8929465
C	-1.0179341	-0.8894767	2.6405007
O	1.9092665	1.4550535	3.4146903
O	3.8877747	-2.6813420	2.7268198
O	0.7024095	-2.2516835	5.4750040
O	0.2365550	-4.4896079	1.6546510
O	-2.1169145	-0.6228629	2.9155563

TS

C	0.8728452	0.0861460	-2.1169231
O	0.3317099	1.3009065	-2.3760463
C	2.3823233	0.2672171	-1.7396572
C	0.8436952	-0.8178128	-3.4224279
F	2.5502359	1.2729425	-0.8520791
F	3.1457661	0.5884037	-2.8224885
F	2.9276035	-0.8539710	-1.1956301
F	1.7061683	-1.8662627	-3.3844497
F	1.1715488	-0.0727099	-4.5093163
F	-0.3875678	-1.3361206	-3.6936514
P	-0.1566360	-0.6142953	-0.5994701
Cl	0.2018391	-2.7260514	-0.7590345
C	-1.7371515	-0.2616717	-1.2558184
H	-1.7652241	-0.7271998	-2.2492046
Si	-1.6300038	1.8899432	-2.0566030
Si	-3.2988604	-0.9482871	-0.4531195
C	-2.1883693	2.7247187	-0.4501238
H	-3.0284257	3.3941005	-0.6988514
H	-1.3746743	3.3579879	-0.0718861

H	-2.5065126	2.0500624	0.3458960
C	-3.0105355	1.4091910	-3.2811098
H	-3.8172166	0.8115725	-2.8387025
H	-2.5632593	0.8173332	-4.0949385
H	-3.4430209	2.3173733	-3.7288437
C	-0.9803045	3.4526730	-2.9683269
H	-0.1158802	3.8911208	-2.4507523
H	-1.7848136	4.2074011	-3.0053138
H	-0.6741084	3.2238617	-3.9993429
C	-4.5937767	0.3360364	0.0520905
H	-4.3066208	0.8696262	0.9676303
H	-5.5438201	-0.1852613	0.2508723
H	-4.7695789	1.0821263	-0.7342725
C	-4.0813488	-2.0419746	-1.7906567
H	-5.0259596	-2.4837137	-1.4375584
H	-3.3937154	-2.8613009	-2.0497607
H	-4.2903723	-1.4775718	-2.7115224
C	-3.0218793	-2.0799879	1.0338038
H	-2.7133854	-1.5373303	1.9348407
H	-2.2580789	-2.8386517	0.8163220
H	-3.9669676	-2.5977372	1.2635792
W	0.4331475	0.1438575	1.8181789
C	0.8119211	2.0741878	1.1949578
C	-1.4628575	0.7139523	2.3262555
C	0.0524020	-1.7703373	2.4694535
C	2.4249851	-0.3782425	1.6563209
C	0.8830391	0.6810396	3.6964457
O	3.5480189	-0.6528502	1.7134760
O	-0.1429611	-2.8346005	2.8825901
O	1.1457841	0.9890338	4.7906906
O	1.0250801	3.1785576	0.9233005
O	-2.4877314	1.0581490	2.7552128

I2

C	2.1130732	0.2647710	-0.9320597
O	1.7523251	1.4871530	-0.3790496
C	3.5991310	0.0462846	-0.4601386
C	2.1568055	0.3943323	-2.5041141
F	3.6671820	-0.3096109	0.8422088

F	4.3280405	1.1930447	-0.5634102
F	4.2417908	-0.8987547	-1.1801641
F	2.3001257	-0.7811481	-3.1406049
F	3.1864587	1.1986144	-2.9122797
F	1.0334732	0.9833331	-2.9901019
P	0.8355721	-1.1206767	-0.2661018
C	-0.5639390	-0.7535472	-1.1206615
Si	0.4888691	2.5783651	-0.1523495
Si	-2.3298199	-1.2319823	-0.9133211
C	-0.6242601	2.1256505	1.2751657
H	-0.0994384	2.1182594	2.2371377
H	-1.0569068	1.1360253	1.0988581
H	-1.4487991	2.8534724	1.3334723
C	-0.5884090	2.8866418	-1.6574064
H	-1.1372419	1.9759582	-1.9292186
H	-0.0132719	3.2253787	-2.5286619
H	-1.3187528	3.6687689	-1.3955872
C	1.4554269	4.1372987	0.2596915
H	2.0978935	3.9624375	1.1343128
H	0.7724560	4.9689182	0.4920497
H	2.0967682	4.4383199	-0.5810642
C	-3.3992867	0.1635179	-0.1959369
H	-3.1994943	0.3258797	0.8715158
H	-4.4682218	-0.0817174	-0.3052007
H	-3.2105946	1.1103309	-0.7241239
C	-2.9882549	-1.5348622	-2.6689668
H	-4.0629568	-1.7746116	-2.6568803
H	-2.4519418	-2.3687630	-3.1453070
H	-2.8469029	-0.6421897	-3.2975499
C	-2.6829477	-2.7893589	0.0919987
H	-2.4662838	-2.6574858	1.1594016
H	-2.0868702	-3.6375716	-0.2703788
H	-3.7497275	-3.0483190	-0.0014190
W	0.8115953	-1.6588838	2.2997032
C	0.7860029	-2.1832398	4.2305261
C	1.6460254	0.1466036	2.8124694
C	2.6872291	-2.5231877	2.1977214
C	0.0826586	-3.5208604	1.7961559
C	-1.0642610	-0.9275647	2.6555444

O	2.1290124	1.1447130	3.1561891
O	3.7135875	-3.0544925	2.2461359
O	0.7704180	-2.4897535	5.3579285
O	-0.2776053	-4.5976574	1.5701668
O	-2.1180887	-0.5607218	2.9856984
H	-0.3947283	-0.4380326	-2.1538185
Cl	1.8970847	-2.9490795	-1.0781749

Final products

C	2.0761514	0.3503113	-0.8353897
O	1.8053238	1.7000061	-0.7472335
C	3.4550731	0.1453064	-0.1293400
C	2.2250718	-0.0418415	-2.3565363
F	3.3467168	0.3986319	1.1986279
F	4.4014529	0.9817471	-0.5978664
F	3.8988254	-1.1260427	-0.2875871
F	2.1930117	-1.3830719	-2.5383198
F	3.3741595	0.4145920	-2.8985522
F	1.2171337	0.5061402	-3.0870549
P	0.7187105	-0.7961919	0.0293240
C	-0.5930064	-0.6854627	-0.9859309
Si	0.5508043	2.7779834	-0.3716544
Si	-2.3819119	-1.2700634	-0.8968767
C	-0.2301391	2.3670754	1.2796914
H	0.5315078	2.2657386	2.0642822
H	-0.8264251	1.4466033	1.2508772
H	-0.9008628	3.1915713	1.5680020
C	-0.7223594	2.8095761	-1.7458626
H	-1.3648065	1.9202270	-1.7374987
H	-0.2370105	2.8764012	-2.7293223
H	-1.3700270	3.6912665	-1.6245956
C	1.4731355	4.4006340	-0.2925389
H	2.2444287	4.3738228	0.4900713
H	0.7833575	5.2273674	-0.0680095
H	1.9668483	4.6167146	-1.2504838
C	-3.3787322	0.0841410	-0.0451598
H	-3.0872163	0.2054088	1.0054655
H	-4.4490497	-0.1709811	-0.0736086
H	-3.2490550	1.0504225	-0.5532134

C	-2.9239748	-1.4002097	-2.6963178
H	-3.9836235	-1.6889969	-2.7583678
H	-2.3348301	-2.1557922	-3.2354680
H	-2.8056283	-0.4400240	-3.2199509
C	-2.6293013	-2.9290777	-0.0582683
H	-2.3654553	-2.9203910	1.0055335
H	-2.0391152	-3.7140574	-0.5496509
H	-3.6918964	-3.2059488	-0.1351102
W	0.8668358	-1.9134142	2.2657029
C	0.8034070	-2.8774168	4.0458951
C	1.4654184	-0.1976617	3.2430014
C	2.8533152	-2.4896283	2.1339487
C	0.3468749	-3.6810201	1.3305550
C	-1.0645533	-1.3480456	2.6574475
O	1.7961645	0.7414595	3.8283887
O	3.9500734	-2.8445238	2.1604575
O	0.7440758	-3.4329599	5.0602099
O	0.0963652	-4.6892948	0.8261534
O	-2.1316093	-1.0207076	2.9671760
H	-0.4236533	-0.1203223	-1.9050423

O	1.3356345	-1.4284564	-0.5716699
O	1.4284564	1.3356345	-0.5716699
O	-1.3356345	1.4284564	-0.5716699
O	-1.4284564	-1.3356345	-0.5716699
C	2.0842901	-0.7731236	0.4513439
C	2.5450989	0.5510754	-0.1384453
C	0.7731236	2.0842901	0.4513439
C	-0.5510754	2.5450989	-0.1384453
C	-2.0842901	0.7731236	0.4513439
C	-2.5450989	-0.5510754	-0.1384453
C	-0.7731236	-2.0842901	0.4513439
C	0.5510754	-2.5450989	-0.1384453
Li	-0.0000000	0.0000000	-1.7141301
H	1.4663359	-0.6036070	1.3541401
H	2.9568798	-1.3845268	0.7508207
H	3.1367413	0.3627068	-1.0449679
H	3.1677786	1.1036261	0.5874330
H	0.6036070	1.4663359	1.3541401

H	1.3845268	2.9568798	0.7508207
H	-0.3627068	3.1367413	-1.0449679
H	-1.1036261	3.1677786	0.5874330
H	-1.4663359	0.6036070	1.3541401
H	-2.9568798	1.3845268	0.7508207
H	-3.1367413	-0.3627068	-1.0449679
H	-3.1677786	-1.1036261	0.5874330
H	-0.6036070	-1.4663359	1.3541401
H	-1.3845268	-2.9568798	0.7508207
H	0.3627068	-3.1367413	-1.0449679
H	1.1036261	-3.1677786	0.5874330
Cl	-0.0000000	0.0000000	-3.8404889

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