Electronic Supplementary Information for manuscript:

Surprising behaviour of M–CO(lone pair)•••π(arene) interactions in the solid state of fluorinated oxaphosphirane complexes

by

Cristina Murcia, Antonio Bauzá, Antonio Frontera* and Rainer Streubel*

Table of content:

1. Experimental methods and synthesis

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 using sodium wire or sodium wire/benzophenone and stored in brown glasses over sodium wire, and under inert gas atmosphere.

Analytical methods

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).

Synthesis of complexes 4b-d.

500 mg (0.75 mmol) of [$(Ph_3CPCl_2)W(CO)_5$] were dissolved in THF (10 mL) and 120 µL (1eq.) of 12-crown-4 were added. The solution was then cooled to -80 °C and 1.2 eq. of ^{t}BuLi (1.7 M in *n*-pentane) was added dropwise. After 5 minutes stirring, 1.2 eq. of the corresponding fluorinated aldehyde were added. The suspension was then stirred for 2 h while gently warming to -20 °C. The solvents were then removed in *vacuo* (*ca.* 0.01 bar) and the residue extracted with 45 mL of *n*-pentane. The product was purified by washing 3 times with 20 mL with *n*-pentane at -30 °C.

4b: Light yellow solid. Yield: 370 mg (0.50 mmol, 74 %). ^{1}H NMR ($CDCl_3$) δ = 4.95 (1H, s, CHP), 6.9 (1H, t, $^3J_{H,H}$ = 8.5 Hz, *p*-Ar^F), 7.1−7.5 (15H, m, 3Ph), 7.6-7.7 (2H, dt, H-Ar^F). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 54.0 (d, $^1J_{C,P}$ = 25.6 Hz, PCO), 67.3 (d, $^1J_{C,P}$ = 6.7 Hz, P-CPh3), 126.3 (s, *p*-Ph), 127.9 (d, $^1J_{C,F}$ = 1.85 Hz, *p*-Ar^F), 128.3 (d, $^3J_{C,P}$ = 5.2 Hz, *m*-Ar^F), 128.7 (s, *m*-Ph), 129.5 (s, *o*-Ph), 130.9 (d, $J_{C,P}$ = 7.3 Hz, *o*-Ph), 139.5 (d, $J_{C,P}$ = 2.4 Hz, *ipso*-Ar^F), 143.9 (s, *ipso*-Ph), 193.8 (d, $^2J_{C,P}$ = 8.1 Hz, *cis*-CO), 195.9 (d, $^2J_{C,P}$ = 41.7 Hz, *trans*-CO). ^{31}P{^{1}H} NMR ($CDCl_3$): 8.9 ppm ($^1J_{W,P}$ = 314 Hz).

4c: Light yellow solid. Yield: 405 mg (0.53 mmol, 81 %). ^{1}H NMR ($CDCl_3$) δ = 5.75 (1H, s, CHP), 7.1−7.5 (15H, m, 3Ph), 7.6-7.7 (2H, dt, H-Ar^F). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 53.4 (d, $^1J_{C,P}$ = 25.7 Hz, PCO), 67.4 (d, $^1J_{C,P}$ = 6.3 Hz, P-CPh3), 126.3 (s, *p*-Ph), 127.9 (d, $^1J_{C,F}$ = 1.85 Hz, *p*-Ar^F), 128.3 (s, *m*-Ph), 128.8 (s, *m*-Ar^F), 129.5 (s, *o*-Ph), 130.9 (d, $J_{C,P}$ = 7.5 Hz, *o*-Ar^F), 139.4 (d, $J_{C,P}$ = 2.5 Hz, *ipso*-Ar^F), 143.9 (s, *ipso*-Ph), 193.9 (d, $^2J_{C,P}$ = 7.9 Hz, *cis*-CO), 195.6 (d, $^2J_{C,P}$ = 41.6 Hz, *trans*-CO). ^{31}P{^{1}H} NMR ($CDCl_3$): 8.5 ppm ($^1J_{W,P}$ = 316 Hz).

4d: Light yellow solid. Yield: 435 mg (0.55 mmol, 87 %). ^{1}H NMR ($CDCl_3$) δ = 7.06−7.72 (15H, m, 3Ph), CHP (was hidden by the trityl signals)). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 53.3 (d, $^1J_{C,P}$ = 24.7 Hz, PCO), 67.6 (d, $^1J_{C,P}$ = 6.6 Hz, P-CPh3),128.1 (d, $J_{C,P}$ = 1.8 Hz, Ph), 128.3 (s, Ph), 128.9 (s, Ph), 129.4

(d, $J_{C,P}$ = 11 Hz, Ar^F), 130.8 (d, $J_{C,P}$ = 7.7 Hz, Ar^F), 139.1 (d, $^3J_{C,P}$ = 2.4 Hz, Ar^F), 193.7 (d, $^2J_{C,P}$ = 8.1 Hz, *cis*-CO), 195.1 (d, $^2J_{C,P}$ = 41.8 Hz, *trans*-CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 7.5 ppm ($^1J_{W,P}$ = 320 Hz).

Single-crystal structure analysis: Crystal structures were recorded on a Nonius Kappa CCD diffractometer and a Nonius MACH3 diffractometer. The structures were solved by Patterson methods or Direct Methods (SHELXS-97)[1] and refined by full-matrix least squares on F^2 (SHELXL-97). All non-hydrogens were refined anisotropically. Hydrogen atoms were included isotropically using the riding model on the bound atoms; in some (denoted) cases hydrogen atoms were located in the Fourier difference electron density. Absorption corrections were carried out analytically or semi-empirically from equivalents. Additionally, some calculation of bond lengths and angles were obtained using the Ortep32 program.[2]

Crystal structure data of complex 4b

Data CCDC: 1035983; Empirical formula: $C_{32}H_{20}Cl_3F_2O_6PW$; Moiety formula: $C_{31}H_{19}F_2O_6PW$ Formula weight: 859.65; Temperature/K: 123.(2); Crystal system: triclinic; Space group: P -1; a/Å: 9.9709(8); b/Å: 10.8286(7); c/Å: 16.0930(15); α/°: 99.983(3); β/°: 98.899(3); γ/°: 109.619(2); Volume/Å: 1568.9(2); Z: 2; ρ_{calc}mg/mm^3: 1.820; m/mm^{-1}: 4.044; F(000): 836; Crystal size/mm^3: 0.27 × 0.25 × 0.10; Θ range for data collection: 2.64 to 27°; Index ranges: $-12 \le h \le 11$, $-13 \le k \le 13$, $-20 \le l \le 20$; Reflections collected: 15563; Independent reflections: 6741; [R_{int} = 0.0260]; Data/restraints/parameters: 6741/0/443; Goodness-of-fit on F^2: 1.058; Final R indexes [I>=2σ (I)]: R_1 = 0.0260, wR_2 = 0.0524; Final R indexes [all data]: R_1 = 0.0354, wR_2 = 0.0563; Largest diff. peak/hole / e Å^{-3}: 1.517/-1.735.

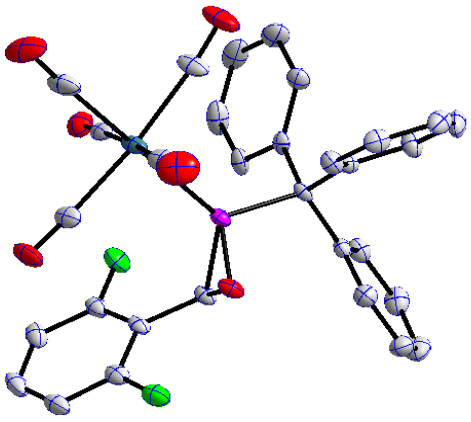

Figure 1. Crystal structure of complex **4b**. Hydrogen atoms were removed for clarity. The crystal structure contains one molecule of $CDCl_3$, which was removed for clarity, per two molecules of **4b**.

Crystal structure data of complex 4c

Data CCDC: 1035984; Empirical formula: $C_{31}H_{18}F_3O_6PW$; Formula weight: 758.27; Temperature/K: 123.15; Crystal system: triclinic; Space group: P -1; a/Å: 10.6619(3); b/Å: 16.0963(4); c/Å: 16.5683(5); α/° : 76.9465(16); β/°: 87.9808(16); γ/°: 86.8159(16); Volume/Å^3: 2764.88(13); Z :4 ; ρ_{calc}mg/mm3: 1.822; m/mm^{-1}: 4.301; F(000):1472 ; Crystal size/mm^3: 0.84 × 0.36 × 0.18; Θ range for data collection: 2.56 to 26°; Index ranges: -12 ≤ h ≤ 13, -19 ≤ k ≤ 19, -18 ≤ l ≤ 20; Reflections collected: 31025; Independent reflections: 10799 [R_{int} = 0.0673]; Data/restraints/parameters: 10799/7/757; Goodness-of-fit on F^2: 1.005; Final R indexes [I>=2σ (I)]: R_1 = 0.0362, wR_2 = 0.0852; Final R indexes [all data]: R_1 = 0.0482, wR_2 = 0.0898; Largest diff. peak/hole / e Å^{-3}: 1.991/-2.996

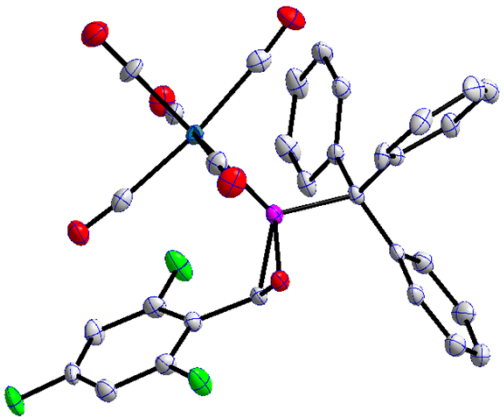

Figure 2. Crystal structure of complex **4c**. Hydrogen atoms were removed for clarity.

Crystal structure data of complex **4d**

Data CCDC: 1035985; Empirical formula: $C_{31}H_{16}F_5O_6PW$; Formula weight: 794.26; Temperature/K: 123.15; Crystal system: monoclinic; Space group: C2/c; a/Å: 36.0465(10); b/Å: 9.5603(3); c/Å: 16.5305(4); α/° : 90.00; β/°: 93.8297(17); γ/°: 90.00; Volume/Å: 35683.9(3); Z : 8; ρ_{calc}mg/mm3: 1.856; m/mm^{-1}: 4.198; F(000): 3072.0; Crystal size/mm^3: 0.16 × 0.12 × 0.04; Radiation: MoKα (λ = 0.71073); 2Θ range for data collection: 4.94 to 56°; Index ranges: -47 ≤ h ≤ 47, -12 ≤ k ≤ 12, -21 ≤ l ≤ 21; Reflections collected: 50383; Independent reflections: 6848 [R_{int} = 0.0952, R_{sigma} = 0.0556]; Data/restraints/parameters: 6848/0/397; Goodness-of-fit on F^2 : 1.024; Final R indexes

[I>=2σ (I)]: R_1 = 0.0378, wR_2 = 0.0857; Final R indexes [all data]: R_1 = 0.0581, wR_2 = 0.0931; Largest diff. peak/hole / e $Å^{-3}$: 3.27/-2.47

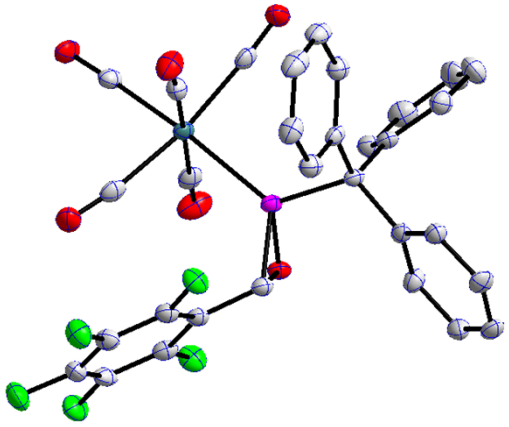

Figure 3. Crystal structure of complex **4d**. Hydrogen atoms were removed for clarity.

2. Figure S1:

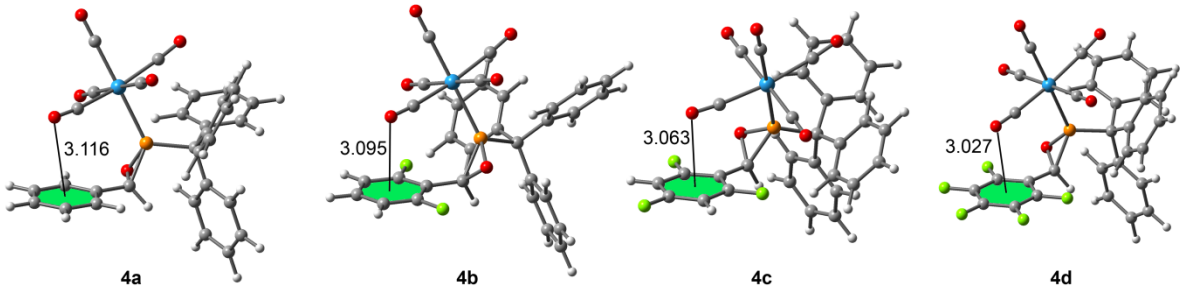

Fig. S1 Optimized complexes **4a-4d** (distances in Å).

3. Figure S2:

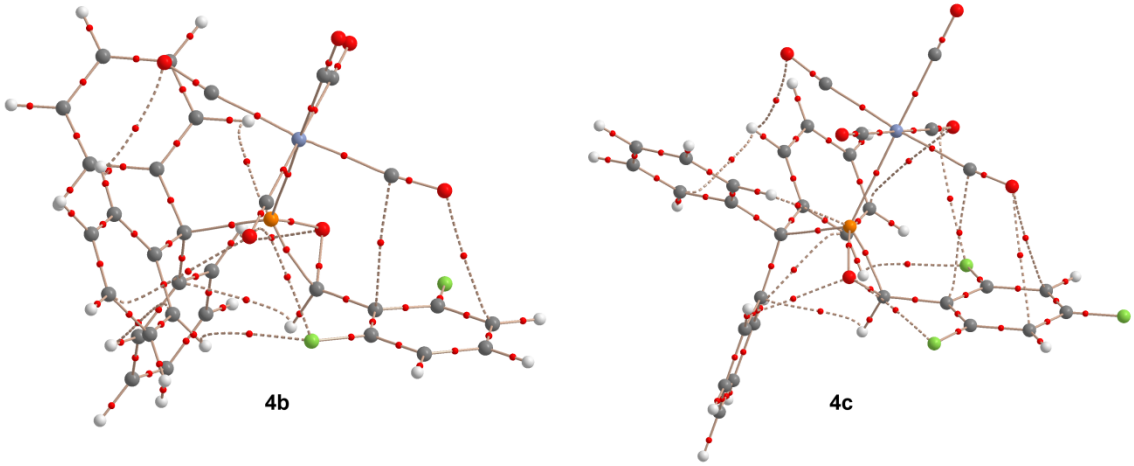

Fig S2. Distribution of critical points in complexes **4b-c** (bond and ring critical points are represented by red and yellow spheres, respectively). Bond paths connecting bond critical points are represented.

2. Computational methods:

The geometries and energies of all complexes included in this study were computed at the BP86-D3/def2-TZVPD level of theory. The optimizations have been performed by using the program TURBOMOLE version 6.4[3] without imposing symmetry constrains The calculation of the wavefunctions that are necessary to carry out the AIM and orbital analyses has been done using the Gaussian-09 program[4] at the BP86/def2-SVP level of theory. The basis set for W atom (def2-SVP) was retrieved from the EMSL basis set exchange.[5] The AIM analysis has been performed using the AIMall program.[6]

3. Cartesian coordinates

4a

C	-1.1334257	-1.0813695	1.3487842
H	-1.2900772	-0.2566608	2.0557379
C	-2.2295088	-2.0695924	1.2310760
C	-1.9693400	-3.4453288	1.2863572
C	-3.0177861	-4.3596816	1.1740156
C	-4.3265326	-3.9097381	0.9890169
C	-4.5890212	-2.5363130	0.9294017
C	-3.5475230	-1.6191711	1.0577071
C	0.7655374	0.9881548	0.2662984
C	0.0035142	1.7568077	-0.8258260
C	-1.3932073	1.9098919	-0.7110169
C	-2.1288935	2.5794071	-1.6872318
C	-1.4889964	3.0965689	-2.8159327
C	-0.1149733	2.9100556	-2.9672768
C	0.6220073	2.2396893	-1.9881331
C	0.5364955	1.5277016	1.6901903
C	-0.1363767	2.7325350	1.9427610
C	-0.2691578	3.2209588	3.2460591
C	0.2679706	2.5159202	4.3234815
C	0.9647243	1.3280104	4.0817451
C	1.1112277	0.8488204	2.7811616
C	2.2857445	0.9336840	0.0666597
C	2.9979879	2.1432980	-0.0069789
C	4.3852548	2.1504783	-0.1368673
C	5.0949593	0.9454442	-0.1761362
C	4.4038423	-0.2602421	-0.0664486
C	3.0117553	-0.2627696	0.0592075
C	0.3379945	-2.9550490	-3.9507632
C	1.7585848	-0.8283060	-2.8261496
C	-1.1081537	-0.5729216	-3.1819595
C	-1.6014257	-3.0277125	-1.9307761
C	1.2686302	-3.3220200	-1.2363862
O	0.2259071	-1.6238757	1.4103801
O	0.4766231	-3.5533103	-4.9344670
O	2.6528283	-0.2343370	-3.2586455
O	-1.8295253	0.1202307	-3.7602162
O	-2.5752996	-3.6497473	-1.9290537
O	1.8994732	-4.1073709	-0.6667722
P	0.0079460	-0.7515540	-0.0158932
W	0.1228079	-1.9227993	-2.2237781
H	-0.9415320	-3.7847841	1.4115235

H	-2.8083263	-5.4291855	1.2162181
H	-5.1426906	-4.6258153	0.8872095
H	-5.6094436	-2.1807682	0.7809451
H	-3.7515112	-0.5472087	1.0122703
H	-3.2076671	2.6874663	-1.5698675
H	-1.9098508	1.5120670	0.1637618
H	-2.0630206	3.6150376	-3.5842517
H	0.3930665	3.2763068	-3.8603077
H	1.6890292	2.0881610	-2.1373484
H	2.4527038	3.0868879	0.0470507
H	4.9160550	3.1015402	-0.1996777
H	6.1805332	0.9500442	-0.2798702
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H	2.4997224	-1.2208237	0.1577772
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H	-0.7915114	4.1642546	3.4128134
H	0.1606012	2.8956255	5.3403296
H	1.4078019	0.7737510	4.9103368
H	1.6792159	-0.0631329	2.6068846

4b

C	-0.7812933	-1.1525563	-1.5106522
H	0.1536817	-1.6480828	-1.8038952
C	-1.7409265	-0.8500263	-2.6060360
C	-2.8028600	-1.6997919	-2.9473501
C	-3.7154781	-1.4031182	-3.9536028
H	-4.5245679	-2.1022476	-4.1578235
C	-3.5635194	-0.2160717	-4.6715891
H	-4.2743215	0.0330257	-5.4590012
C	-2.5091324	0.6553198	-4.3913202
H	-2.3662393	1.5881737	-4.9339728
C	-1.6273765	0.3166994	-3.3741652
C	1.0309583	-0.3167383	0.7101539
C	1.8101355	-1.5317995	0.1820842
C	3.0617845	-1.4052824	-0.4394350
H	3.4929650	-0.4184002	-0.5993368
C	3.7793449	-2.5350738	-0.8424174
H	4.7532636	-2.4088946	-1.3178321
C	3.2605314	-3.8134412	-0.6332950
H	3.8183995	-4.6945402	-0.9529425
C	2.0263223	-3.9530537	0.0081061
H	1.6152867	-4.9455266	0.1975732
C	1.3175926	-2.8273904	0.4248160
H	0.3710681	-2.9550846	0.9468516
C	0.9765478	-0.4663809	2.2354795
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C	-0.1713424	-1.0758302	4.2958870
H	-1.0842857	-1.4036472	4.7940833
C	0.9885123	-0.8332899	5.0307320
H	0.9908568	-0.9626339	6.1135542
C	2.1541438	-0.4374923	4.3653907
H	3.0738398	-0.2668131	4.9267280
C	2.1492585	-0.2642210	2.9825001
H	3.0665445	0.0264000	2.4680433

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H	1.5708070	0.4521075	-1.8621673
C	2.1460294	2.5043089	-1.6452208
H	2.2765729	2.6409333	-2.7190598
C	2.3557206	3.5703215	-0.7679964
H	2.6591422	4.5456596	-1.1495233
C	2.1460374	3.3806635	0.5981229
H	2.2828741	4.2083002	1.2951068
C	1.7465339	2.1353177	1.0874070
H	1.5765463	2.0171614	2.1547912
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C	-1.3750498	2.9768493	-0.5433129
C	-1.2385928	2.2013273	2.3216970
C	-3.2996845	0.2533671	1.8862426
C	-3.6570304	1.1355230	-0.8311081
O	-1.3491258	-1.7290895	-0.2827324
O	-4.4336348	3.8758325	1.5096700
O	-0.8722197	3.7572167	-1.2298672
O	-0.7025570	2.5632990	3.2812146
O	-3.8271933	-0.5170045	2.5700799
O	-4.4776190	0.9203866	-1.6174312
F	-2.9418300	-2.8638302	-2.2740531
F	-0.5992936	1.1607026	-3.0993378
P	-0.7497606	-0.1841459	0.0060039
W	-2.3429753	1.6207251	0.6828796

4c

C	0.9617020	0.8967302	1.5721267
H	0.5769170	0.2458047	2.3676379
C	2.3495250	1.4025754	1.7419589
C	2.6458800	2.6606359	2.2862611
C	3.9398459	3.1507708	2.4206680
H	4.1240201	4.1390542	2.8352679
C	4.9815071	2.3306250	2.0027669
C	4.7742359	1.0603941	1.4749069
H	5.6004645	0.4327070	1.1501148
C	3.4579461	0.6343555	1.3624303
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H	-1.8692001	1.9279745	-0.7938672
C	-3.7886912	1.5530514	-1.6691661
H	-3.9309731	2.6000337	-1.9390020
C	-4.7748477	0.6090847	-1.9526481
H	-5.6955826	0.9089895	-2.4541957
C	-4.5805561	-0.7236410	-1.5731885
H	-5.3544278	-1.4672295	-1.7686398
C	-3.4019378	-1.1076867	-0.9366727
H	-3.2656669	-2.1443042	-0.6252456

C	-0.3717138	-1.7943725	-0.5837535
C	-0.6914199	-2.2792727	-1.8602396
H	-1.5351057	-1.8608697	-2.4038882
C	0.0690759	-3.2881211	-2.4563596
H	-0.2016042	-3.6418123	-3.4519496
C	1.1708407	-3.8299616	-1.7935716
H	1.7676328	-4.6119248	-2.2639565
C	1.5178820	-3.3408038	-0.5322694
H	2.3931811	-3.7307284	-0.0122270
C	0.7621621	-2.3306459	0.0592012
H	1.0623647	-1.9513741	1.0349718
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C	-1.4919650	-2.1751338	2.1111801
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C	0.0552726	3.1215225	-2.1702905
C	2.7253614	2.4834410	-1.3234560
C	2.3935703	-0.2730215	-2.3047854
C	-0.2628064	0.5350967	-3.3722807
F	1.6290788	3.4402146	2.7080120
F	6.2492765	2.7847433	2.1180243
F	3.2315196	-0.5973980	0.8436918
O	-0.0398818	1.8751437	1.1272184
O	2.4894941	2.3923823	-4.9988802
O	-0.6053555	4.0708001	-2.1334512
O	3.5834404	3.1387123	-0.9070507
O	3.0826439	-1.1978219	-2.3626346
O	-1.0707805	0.1048595	-4.0796900
P	0.2272317	0.7167857	-0.0622645
W	1.2160490	1.4251092	-2.2454510

4d.

W	-0.9741280	1.8560554	2.0639783
P	-0.0081917	0.7542597	0.0440618
F	-2.9785828	0.1396308	-2.0235587
F	-5.1245639	1.6818902	-2.6744100

F	-4.8044990	4.3750931	-3.0469226
F	-2.3305842	5.5085797	-2.7778998
F	-0.1935768	3.9948783	-2.1551023
O	0.7849386	1.6980798	-1.1080634
O	-2.0065727	3.4093860	4.6451050
O	0.8247920	0.1804827	4.1383332
O	-3.3681304	-0.2638640	2.4229699
O	-3.1193469	3.6610890	0.4933265
O	1.3179639	4.0829290	1.6914059
C	-0.4078417	1.1010769	-1.6883596
H	-0.1894155	0.3055764	-2.4113305
C	-1.5227766	2.0118656	-2.0545343
C	-2.8035404	1.4667474	-2.2111812
C	-3.9119415	2.2397133	-2.5425350
C	-3.7495022	3.6150075	-2.7317429
C	-2.4855785	4.1896857	-2.5935704
C	-1.3874978	3.3910465	-2.2620748
C	0.8744549	-0.9446956	0.0923598
C	1.3209054	-1.4223411	-1.2998575
C	0.8552694	-2.6105064	-1.8827498
H	0.1348988	-3.2319827	-1.3542600
C	1.3195198	-3.0244086	-3.1351921
H	0.9440019	-3.9549919	-3.5632582
C	2.2580359	-2.2607163	-3.8298266
H	2.6131862	-2.5807235	-4.8101707
C	2.7530851	-1.0909219	-3.2450525
H	3.5037986	-0.4932251	-3.7638360
C	2.3030228	-0.6859221	-1.9896616
H	2.7172603	0.2135784	-1.5382040
C	-0.2477763	-1.7811134	0.7304112
C	-1.4476316	-1.9775128	0.0183858
H	-1.5581729	-1.5596237	-0.9821250
C	-2.5020972	-2.7039967	0.5693947
H	-3.4184737	-2.8409041	-0.0051785
C	-2.3905329	-3.2336289	1.8569635
H	-3.2169583	-3.7946284	2.2939806
C	-1.2259164	-3.0068456	2.5913716
H	-1.1373073	-3.3871356	3.6097527
C	-0.1671770	-2.2838890	2.0370452
H	0.7253358	-2.1068514	2.6329708
C	2.1479096	-0.8486066	0.9446549
C	2.7179787	0.3652824	1.3418407
H	2.2448455	1.3115970	1.0785999
C	3.9085569	0.3955457	2.0741586

H	4.3275109	1.3555464	2.3774015
C	4.5545494	-0.7935431	2.4089422
H	5.4815526	-0.7731069	2.9830577
C	4.0115788	-2.0133547	1.9897617
H	4.5184409	-2.9493859	2.2281370
C	2.8267160	-2.0385387	1.2580171
H	2.4188683	-2.9907947	0.9154836
C	-1.6409367	2.8371478	3.7064230
C	0.2101967	0.7605220	3.3492356
C	-2.4833037	0.4635511	2.2768769
C	-2.3102160	2.9980116	0.9901901
C	0.4935973	3.2839043	1.8260611

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