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Electronic Supplementary Information for manuscript:

On the nature of M–CO(lone pair)···π(arene) interactions in the solid state of fluorinated oxaphosphirane complexes

by

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Table of content:

1. AIM analysis for complexes 11 to 13

The distribution of critical points and bond paths for complexes 11–13 are shown in Figure S1. All complexes are characterized by the presence of two bond critical points that connect the two ends of the C≡O with two carbon atoms of the aromatic ring. The interaction is further characterized by the presence of two ring and one cage CP (yellow and green spheres, respectively, see Fig. S1). The charge density (ρ) computed at the bond CPs can be used as a measure of bond order. Using complex **13** as model (π-neutral) for comparison purposes, it can be observed that complex **11** presents larger ρ value at the bond CP that connects the O atom with the ring and smaller ρ value at the bond CP that connects the C atom with the ring than complex **13**, indicating that the O···π strengthens and the C···π weakens with respect to **13**. Interestingly, the contrary is found in complex **12**, where the O···π weakens and the O···π strengthens.

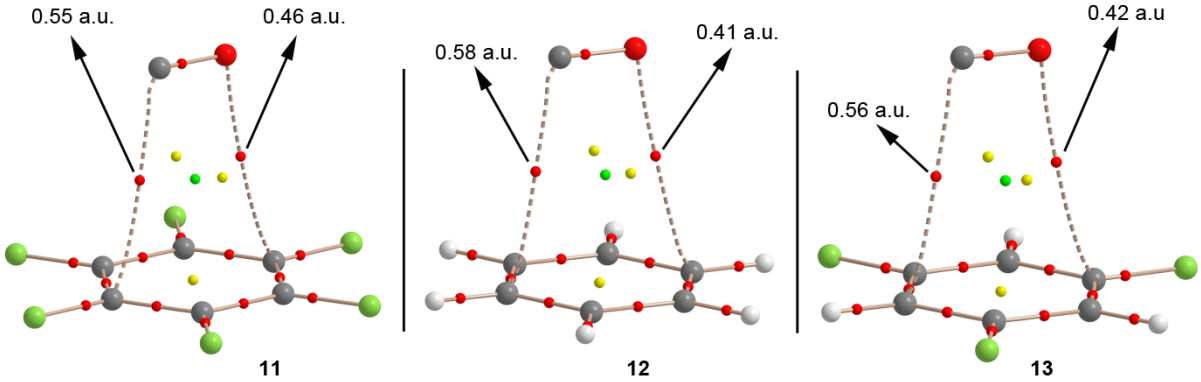

Fig. S1 Distribution of bond, ring and cage critical points (red, yellow and green spheres, respectively) and bond paths for complexes **11-13** at the BP86-D3/def2-TZVP level of theory. The density ($\times 10^2$) at the bond critical points are indicated in a.u.

2. CSD codes intermolecular search

TIHPOR	BERYIG	CACLUN	CAQCOM	CAZMUL
CEMROC	CUMVOV	DEKMUB01	DEPRIA	DOGNAO
DUWNEP	ELACAV	FODHIP	FOHYAD	GEMMAM
HIBNIP	IFEBOK	IGICUW	IXUWON	JOXYOK
JUCYIP	JUPYIC	JUPYOI	JURNAL	KAVWIN
KESRAB	LAZSOV	LEBSIU	LESXIQ	MOJXUF
MOWFIN	MUVDAJ	NAVFEV	NIQNAC	NUSZAC
OCUTIQ	ODENOA	PAHPET	POQQOB	QOGCOE
MOZFIS	SOTFUE	BODNOX	FUBTAX	NESMON
PUHHIJ	WUGWOK	XUZZOH		

2. CSD codes intramolecular search

BIMHEM	COLJIY	ATAZAW	BAPLEL	BAVJAK
BENQES	BODRIV	CAQYEZ	CIPPAS	CIPPAS10
CIPWPB	COPYEL	COWFIE	CUWQAM	DAFMUT
DAYBUA	DIKJIQ	DOGNAO	DOGNIW	DOXDAW
DUWNEP	ESODEW	FAVXAC	FAZNEZ	FIDXUM
FOFKAM	GABWIR	GENNUK	GENPAS	GIBLOT
GIBMAG	HEFKAG	HEYZES	IMOWAI	IMOWEM
ITISEK	JEDLAF	JIXSUE	KESPUT	KIHSUP
KIPVAI	KUHSOW	LAZSEL	LEGYIF	LUKXEU
MABKAD	MACXOE	MEDRES	MIGWEE	MOXMIW
NEVSOW	NIQNAC	OFAJAI	PASVIO	PIXQES
POBVOR	POBVOR10	POBVOR11	POXVOO	PUKXOI
QAWRIP	RIFMUO	RISGOP	RURGIU	SANGIX
SANHAQ	SANWIN	SANWOT	SICBUD	SUKSAT
TALPUR	TAXJIM	TAZDEF	UDIFET	UMIFUR
VAGBAG	VAGBAG10	VALCUH	VAVMUA	VECHES
VECHUI	VECJAQ	VIKDEA	VOSPOI	WIYQIE
WOGFOO	XAFPUQ	XAFQAX	XODDAW	XOHDIH
YARBUO	YATFAB	YUBHEI	ZEYJOC	ZIDTEL
MOZFEO	MOZFIS	SOMRAP		

4. Theoretical models of the assemblies of 1 and 4

In Figure S1 we show the theoretical models used to calculate the supramolecular assemblies computed for compounds **1** and **4** to study the influence of the crystal packing on the W–CO···π distance. In both assemblies we have replaced the phenyl rings that do not participate in the formation of the assembly by hydrogen atoms, in order to keep the size of the systems computationally approachable. Similarly, in two oxaphosphirane complexes we have eliminated the $W(CO)_5$ moieties because they do not participate in the assembly.

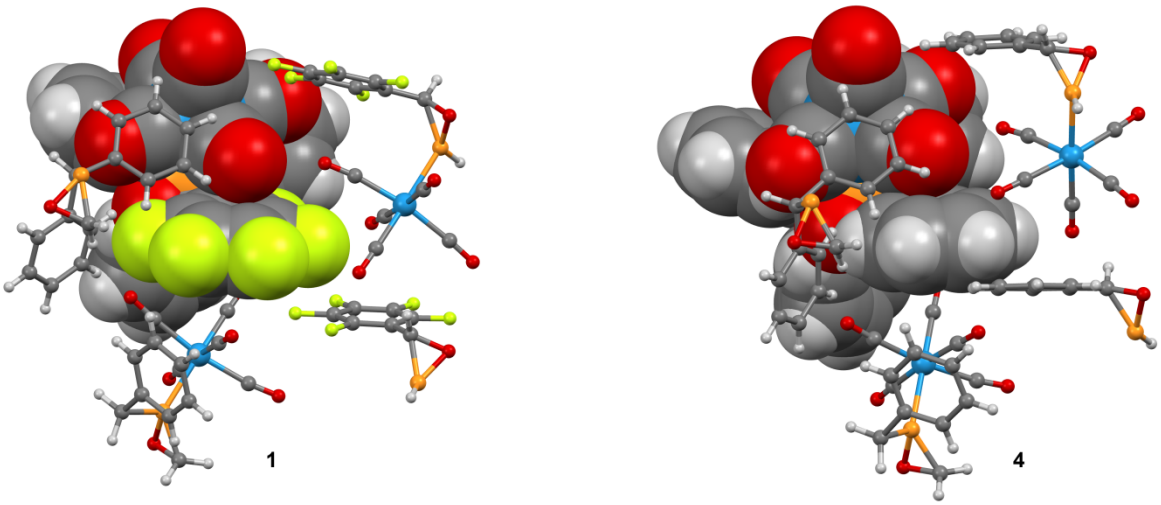

Fig S2. Optimized theoretical models used to simulate the X-ray assemblies of compounds **1** and **4**.

5. Cartesian coordinates for complexes 5 to 19

5.

C	-1.2102243	0.6987233	0.5239710
C	-1.2102243	-0.6987233	0.5239710
C	0.0000000	-1.3974467	0.5239710
C	1.2102243	-0.6987233	0.5239710
C	1.2102243	0.6987233	0.5239710
C	0.0000000	1.3974467	0.5239710
F	-2.3713851	1.3691198	0.5176798
F	-2.3713851	-1.3691198	0.5176798
F	0.0000000	-2.7382397	0.5176798
F	2.3713851	-1.3691198	0.5176798
F	2.3713851	1.3691198	0.5176798
F	0.0000000	2.7382397	0.5176798
C	0.0000000	0.0000000	-3.6934328
O	-0.0000000	-0.0000000	-2.5564717

6.

C	-1.2104032	0.6988266	0.5320567
C	-1.2104032	-0.6988266	0.5320567
C	0.0000000	-1.3976532	0.5320567
C	1.2104032	-0.6988266	0.5320567
C	1.2104032	0.6988266	0.5320567
C	0.0000000	1.3976532	0.5320567
H	-2.1554088	1.2444258	0.5313661
H	-2.1554088	-1.2444258	0.5313661
H	-0.0000000	-2.4888517	0.5313661
H	2.1554088	-1.2444258	0.5313661
H	2.1554088	1.2444258	0.5313661
H	-0.0000000	2.4888517	0.5313661
C	0.0000000	0.0000000	-3.7581389
O	0.0000000	-0.0000000	-2.6223981

7.

C	-0.7069516	1.2244761	0.5294430
C	-1.3689461	0.0000000	0.5287663
C	-0.7069516	-1.2244761	0.5294430
C	0.6844731	-1.1855421	0.5287663
C	1.4139032	0.0000000	0.5294430
C	0.6844731	1.1855421	0.5287663
H	-1.2505925	2.1660898	0.5266165
H	-1.2505925	-2.1660898	0.5266165
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C	0.0000000	0.0000000	-3.7300019
O	0.0000000	0.0000000	-2.5936751
F	-2.7231243	0.0000000	0.5230665
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F	1.3615621	-2.3582948	0.5230665

8.

C	-1.2100769	0.6986382	0.5469964

C	-1.2100769	-0.6986382	0.5469964
C	0.0000000	-1.3972764	0.5469964
C	1.2100769	-0.6986382	0.5469964
C	1.2100769	0.6986382	0.5469964
C	0.0000000	1.3972764	0.5469964
F	-2.3713630	1.3691071	0.5409560
F	-2.3713630	-1.3691071	0.5409560
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F	2.3713630	-1.3691071	0.5409560
F	2.3713630	1.3691071	0.5409560
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C	0.0000000	0.0000000	-2.6959164

9.

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C	-1.210353	-0.698797	0.549916
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C	1.210353	-0.698797	0.549916
C	1.210353	0.698797	0.549916
C	0.000000	1.397595	0.549916
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H	-2.155362	-1.244399	0.548991
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H	2.155362	-1.244399	0.548991
H	2.155362	1.244399	0.548991
H	0.000000	2.488798	0.548991
O	0.000000	0.000000	-3.865612
C	0.000000	0.000000	-2.727829
X	0.000000	0.000000	0.549916

10.

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C	1.4138766	0.0000000	0.5499897
C	0.6843499	1.1853288	0.5493879
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H	-1.2505631	-2.1660389	0.5479032
H	2.5011263	0.0000000	0.5479032
F	-2.7230306	0.0000000	0.5444458
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F	1.3615153	-2.3582137	0.5444458
O	-0.0000000	0.0000000	-3.8559797
C	0.0000000	0.0000000	-2.7192002

11.

C	-0.4877046	-0.6844250	1.2107891
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C	-0.4233070	1.4110021	0.0000000
C	-0.4441946	0.7124504	-1.2111063
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F	-0.5400936	-2.7215515	0.0000000
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F	-0.5019913	-1.3566598	-2.3699844

12.

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H	-0.4116149	1.2484303	-2.1556684
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13.

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C	-0.4151395	0.7119427	-1.1860549
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F	-0.6795364	-2.6839386	0.0000000
F	-0.3583452	1.3876412	-2.3574690
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H	-0.5665616	-1.2179352	-2.1659547

14.

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C	0.9882739	-0.9889042	3.2403530
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C	0.3616677	1.3490773	3.2396040
C	-0.9882739	0.9889042	3.2403530
W	0.0000000	-0.0000000	-2.9867821
C	-1.4522504	-1.4785759	-2.9857184
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C	1.4522504	1.4785759	-2.9857184

C	-1.4785696	1.4522500	-2.9857232
C	0.0000000	-0.0000000	-0.9228184
O	0.0000000	-0.0000000	0.2321273
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O	2.3010146	-2.2600965	-2.9829918
O	0.0000000	-0.0000000	-6.2139791
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O	-2.3010146	2.2600965	-2.9829918
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F	-2.6441648	-0.7082140	3.2306861
F	-1.9361516	1.9374710	3.2331393
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F	1.9361516	-1.9374710	3.2331393

15.

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C	-0.3619803	-1.3502887	3.3063491
C	0.9883488	-0.9885033	3.3062981
C	1.3503444	0.3617662	3.3063500
C	0.3619803	1.3502887	3.3063491
C	-0.9883488	0.9885033	3.3062981
H	-2.4043209	-0.6440500	3.3060860
H	-0.6444298	-2.4042188	3.3060833
H	1.7598699	-1.7601463	3.3059315
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H	0.6444298	2.4042188	3.3060833
H	-1.7598699	1.7601463	3.3059315
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C	1.4771876	-1.4516234	-3.0523141
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C	0.0000000	-0.0000000	-0.9769792
O	0.0000000	-0.0000000	0.1742147
O	-2.2601110	-2.2998985	-3.0526386
O	2.2999025	-2.2601188	-3.0526185
O	0.0000000	-0.0000000	-6.2760405
O	2.2601110	2.2998985	-3.0526386
O	-2.2999025	2.2601188	-3.0526185

16.

C	-0.6895580	-3.2699196	-1.1851723
C	0.7015310	-3.2660655	-1.2245210
C	1.3629269	-3.2627409	0.0000000
C	0.7015310	-3.2660655	1.2245210
C	-0.6895580	-3.2699196	1.1851723
C	-1.4185527	-3.2732843	0.0000000
W	0.0060740	3.0163779	0.0000000
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C	2.0779196	3.0253317	0.0000000
C	0.0003110	5.0883587	0.0000000

C	0.0003734	3.0143551	2.0716978
C	-2.0654751	3.0034252	0.0000000
C	0.0196179	0.9464028	0.0000000
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O	-0.0066972	3.0117081	-3.2247341
O	3.2309714	3.0294137	0.0000000
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O	-0.0066972	3.0117081	3.2247341
O	-3.2185081	2.9941089	0.0000000
F	-1.3686006	-3.2669258	-2.3572988
F	-1.3686006	-3.2669258	2.3572988
F	2.7174250	-3.2515537	0.0000000
H	1.2450164	-3.2610880	2.1663957
H	-2.5057963	-3.2749266	0.0000000
H	1.2450164	-3.2610880	-2.1663957

17.

C	-0.492920	-3.314203	-1.210651
C	0.656666	-2.520430	-1.210329
C	1.232039	-2.126681	0.000000
C	0.656666	-2.520430	1.210329
C	-0.492920	-3.314203	1.210651
C	-1.066034	-3.712493	0.000000
F	-1.047867	-3.690589	-2.371204
F	-2.169305	-4.472626	0.000000
F	-1.047867	-3.690589	2.371204
F	1.198402	-2.121648	-2.370481
F	2.327500	-1.353281	0.000000
F	1.198402	-2.121648	2.370481
W	-0.067313	2.668468	0.000000
C	-0.054525	2.649707	-2.071528
C	1.881904	1.958030	0.000000
C	0.678459	4.603147	0.000000
C	-0.054525	2.649707	2.071528
C	-1.981374	3.456925	0.000000
C	-0.892512	0.775993	0.000000
O	-1.393351	-0.264949	0.000000
O	-0.042485	2.630685	-3.224118
O	2.980159	1.610310	0.000000
O	1.078542	5.684074	0.000000
O	-0.042485	2.630685	3.224118
O	-3.043254	3.906037	0.000000

18.

C	-0.429521	-3.031945	-1.210900
C	0.776223	-2.324966	-1.211104
C	1.381686	-1.976180	0.000000
C	0.776223	-2.324966	1.211104
C	-0.429521	-3.031945	1.210900
C	-1.030620	-3.387694	0.000000
H	-0.902695	-3.304478	-2.155496
H	1.248497	-2.049418	-2.155374
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H	1.248497	-2.049418	2.155374

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H   -0.902695   -3.304478    2.155496
H   -1.973882   -3.935956    0.000000
W   -0.146948    2.450723    0.000000
C   -0.149899    2.415392   -2.069722
C    1.703992    1.529085    0.000000
C    0.818911    4.277965    0.000000
C   -0.149899    2.415392    2.069722
C   -1.945914    3.474771    0.000000
C   -1.212367    0.666956    0.000000
O   -1.870607   -0.277022    0.000000
O   -0.154664    2.380288   -3.222731
O    2.764068    1.072830    0.000000
O    1.344264    5.305383    0.000000
O   -0.154664    2.380288    3.222731
O   -2.936407    4.065861    0.000000
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19.

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C 0   -0.626139   -3.468210   -1.185886
C 0    0.739375   -3.200362   -1.224836
C 0    1.387095   -3.072434    0.000000
C 0    0.739375   -3.200362    1.224836
C 0   -0.626139   -3.468210    1.185886
C 0   -1.341188   -3.608293    0.000000
F 0   -1.290622   -3.599257   -2.358753
F 0   -1.290622   -3.599257    2.358753
F 0    2.715896   -2.809896    0.000000
H 0    1.276222   -3.097904   -2.164961
H 0    1.276222   -3.097904    2.164961
H 0   -2.407865   -3.816839    0.000000
W 0   -0.043387    3.079146    0.000000
C 0   -0.045294    3.080251   -2.071472
C 0    2.001819    2.752541    0.000000
C 0    0.287660    5.123713    0.000000
C 0   -0.045294    3.080251    2.071472
C 0   -2.088672    3.407790    0.000000
C 0   -0.367018    1.032133    0.000000
O 0   -0.544419   -0.107071    0.000000
O 0   -0.047644    3.082065   -3.224656
O 0    3.140614    2.572190    0.000000
O 0    0.474790    6.262061    0.000000
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