Electronic Supplementary Information

"Synthesis and DFT Calculations of Spirooxaphosphirane Complexes"

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Content:

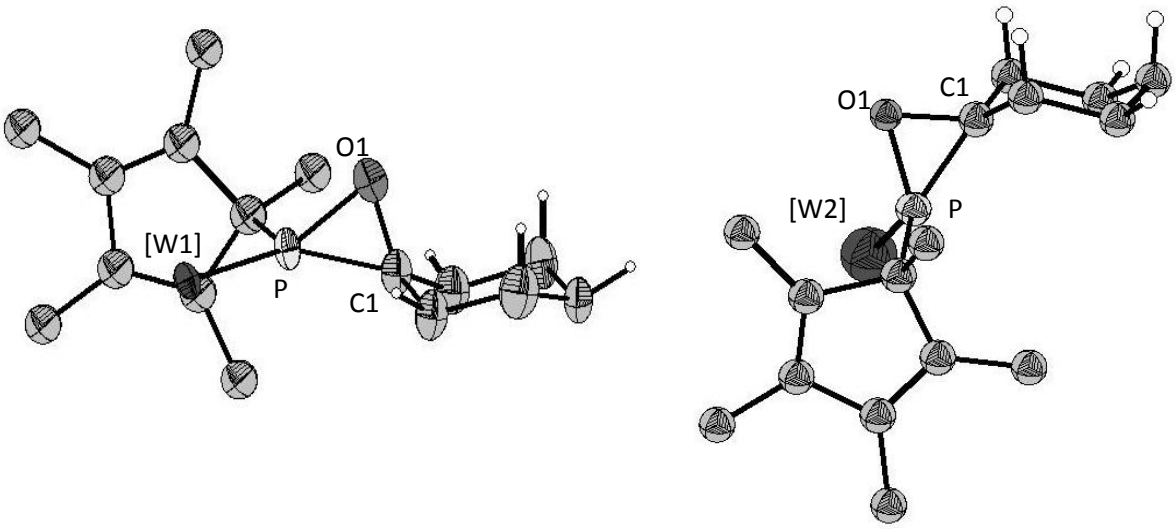

Figure S1: Reduced formulas of both observed chair confirmations in crystals of **9a,a'**.

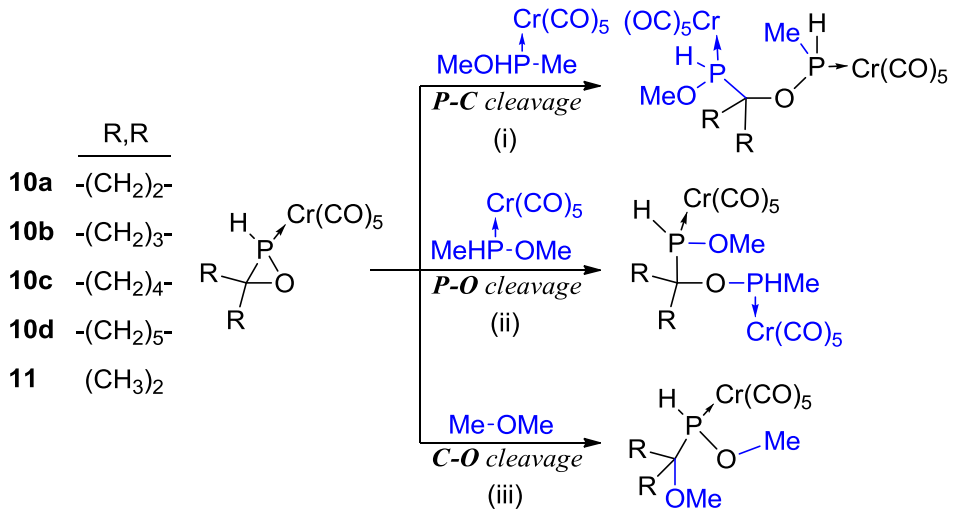

Figure S2: Homodesmotic reactions used for the calculation of RSEs.

Cartesian coordinates (Å) and energies (au) for all computed species.

Complex **10a**: E = -2142.341133595 au (SCS-MP2/def2-TZVPPecp)

C	0.252416	-0.148158	0.077708	C	1.905712	4.249539	-3.085201
O	1.689218	-0.036091	0.160858	O	2.202004	5.027602	-3.867317
P	0.959693	1.454369	-0.069195	C	0.859451	4.380816	-0.648977
C	-0.614019	-1.012946	0.899047	O	0.492625	5.256807	-0.015394
H	-1.525596	-0.594789	1.310394	C	3.237906	3.070820	-1.079380
H	-0.122457	-1.752498	1.520378	O	4.306649	3.151811	-0.689742
C	-0.515074	-1.194954	-0.622320	C	2.014073	1.523420	-2.925801
H	-1.361560	-0.901914	-1.230525	O	2.346594	0.682299	-3.618516
H	0.046355	-2.050161	-0.980471	C	-0.325134	2.802312	-2.452088
H	0.835914	1.951397	1.252832	O	-1.397073	2.713868	-2.836934
Cr	1.453066	2.954024	-1.767651				

Complex **10b**: E = -2181.585348574 au (SCS-MP2/def2-TZVPPecp)

C	-0.069250	0.015322	0.164313	H	1.751909	1.507745	1.070626
O	-0.053739	0.003231	1.616762	Cr	3.135485	-1.475489	1.310166
P	1.494309	0.115758	1.011956	C	4.487975	-2.799215	1.492169
C	-0.842279	1.039916	-0.660636	O	5.296949	-3.600985	1.579993
H	-0.317596	1.942968	-0.974802	C	4.442091	-0.183978	0.758341
H	-1.768312	1.317627	-0.150553	O	5.213518	0.590193	0.424849
C	-1.058966	-0.084226	-1.717382	C	3.332570	-0.927249	3.143945
H	-0.350730	-0.012752	-2.542106	O	3.438041	-0.609760	4.234957
H	-2.067132	-0.186359	-2.115873	C	1.781783	-2.721202	1.880945
C	-0.624666	-1.142387	-0.661007	O	0.974888	-3.450611	2.222931
H	0.065931	-1.924099	-0.974512	C	2.889000	-2.019470	-0.506943
H	-1.478732	-1.593218	-0.149577	O	2.732836	-2.340151	-1.592919

Complex **10c**: E = -2220.842143914 au (SCS-MP2/def2-TZVPPecp)

C	0.054426	-0.013334	-0.076197	H	-0.028989	2.091313	-0.718619
O	-0.065774	-0.218055	1.376430	H	-1.449758	1.474800	0.124842
P	1.521913	0.003997	0.943132	C	-1.317341	0.754432	-1.926827
C	-0.676812	1.221428	-0.606479	H	-0.608794	0.878149	-2.751040

H	-2.217451	1.317997	-2.175935	O	5.338725	-3.552630	2.149156
C	-1.583771	-0.740362	-1.690544	C	4.497740	-0.235984	0.838138
H	-1.763647	-1.294537	-2.612797	O	5.265430	0.542671	0.505713
H	-2.456714	-0.866395	-1.044210	C	3.245471	-0.860558	3.170077
C	-0.317799	-1.207836	-0.951346	O	3.284548	-0.464586	4.240250
H	0.481633	-1.401601	-1.671380	C	1.854105	-2.816852	1.902760
H	-0.454699	-2.105696	-0.348229	O	1.068805	-3.584092	2.211102
H	1.722151	1.384651	1.191394	C	3.133939	-2.176794	-0.419084
Cr	3.193825	-1.534426	1.382627	O	3.107713	-2.542186	-1.501283
C	4.542973	-2.791671	1.842968				

Complex **10d**: E = -2260.075062258 au (SCS-MP2/def2-TZVPPecp)

C	-0.189487	-0.496298	-0.213985	C	0.100805	-1.304856	-1.458031
O	-0.463603	-1.278731	0.989683	H	0.830208	-2.088398	-1.249287
P	1.001171	-0.497162	1.129851	H	-0.830466	-1.799422	-1.759385
C	-1.154978	0.643162	-0.427168	H	0.665988	0.673035	1.854555
H	-1.291853	1.201502	0.501224	Cr	2.905464	-1.769028	1.537044
H	-2.122370	0.193558	-0.686122	C	4.315276	-2.951797	1.978742
C	-0.684159	1.554333	-1.566353	O	5.144689	-3.681965	2.271580
H	0.230810	2.069801	-1.255417	C	3.433188	-1.695631	-0.304971
H	-1.438435	2.321824	-1.755138	O	3.755213	-1.634774	-1.399761
C	-0.406860	0.751650	-2.842461	C	4.063115	-0.279113	1.850778
H	-0.026361	1.413653	-3.624151	O	4.804409	0.573412	2.021747
H	-1.347959	0.324356	-3.208564	C	2.377257	-1.761040	3.382042
C	0.589699	-0.381764	-2.582108	O	2.076231	-1.748653	4.483501
H	1.556590	0.045865	-2.297006	C	1.821315	-3.299375	1.155261
H	0.752905	-0.967392	-3.489487	O	1.200426	-4.222640	0.907800

Complex **11**: E = -2143.598288536 au (SCS-MP2/def2-TZVPPecp)

C	0.010293	0.014484	-0.006593	Cr	1.557866	2.965525	-1.687678
O	1.462349	0.022043	0.268775	C	2.058597	4.069723	-3.141663
P	0.900762	1.566297	0.037882	O	2.368849	4.732442	-4.019138
C	-0.806026	-0.450239	1.170180	C	-0.193922	2.723123	-2.424618
H	-0.451526	0.002622	2.097062	O	-1.255965	2.576937	-2.820080
H	-0.726666	-1.538590	1.261981	C	0.914239	4.505348	-0.745260
H	-1.857277	-0.186893	1.027565	O	0.524333	5.434693	-0.207469
C	-0.339656	-0.597569	-1.339517	C	3.302869	3.218178	-0.923972
H	0.222462	-0.150057	-2.156318	O	4.354139	3.388553	-0.514157
H	-0.110385	-1.667739	-1.314050	C	2.240979	1.426392	-2.610267
H	-1.405806	-0.466329	-1.538995	O	2.667724	0.514686	-3.147058
H	0.663657	2.022188	1.358714				

Complex **12c**: E = -1208.228138407 au ($COSMO_{THF}$/B3LYP-D3/def2-TZVPPecp)

C	-0.093129	0.031708	0.039887	O	1.732374	5.387219	-4.068543
O	1.387570	-0.044469	-0.082661	C	0.526987	4.675732	-0.502362
P	0.885624	1.536588	0.048643	O	0.135875	5.474990	0.219545
C	-0.799311	-0.354938	-1.235604	C	3.149230	3.495295	-1.080617
H	-1.852625	-0.075181	-1.180366	O	4.212852	3.652241	-0.686598
H	-0.356493	0.125497	-2.106436	C	1.902763	1.718438	-3.053396
H	-0.736794	-1.438124	-1.371062	O	2.274065	0.892694	-3.752181
C	-0.642179	-0.619366	1.282479	C	-0.709583	2.940867	-2.486607
H	-0.608719	-1.705992	1.162636	O	-1.778175	2.800541	-2.872152
H	-1.684411	-0.326317	1.422074				
H	-0.083803	-0.361110	2.178885				
C	1.257302	2.079000	1.743285				
H	2.281469	2.456166	1.757359				
H	1.155143	1.281713	2.474924				
H	0.586006	2.903206	1.992852				
W	1.223393	3.217003	-1.790377				
C	1.546350	4.606627	-3.246709				

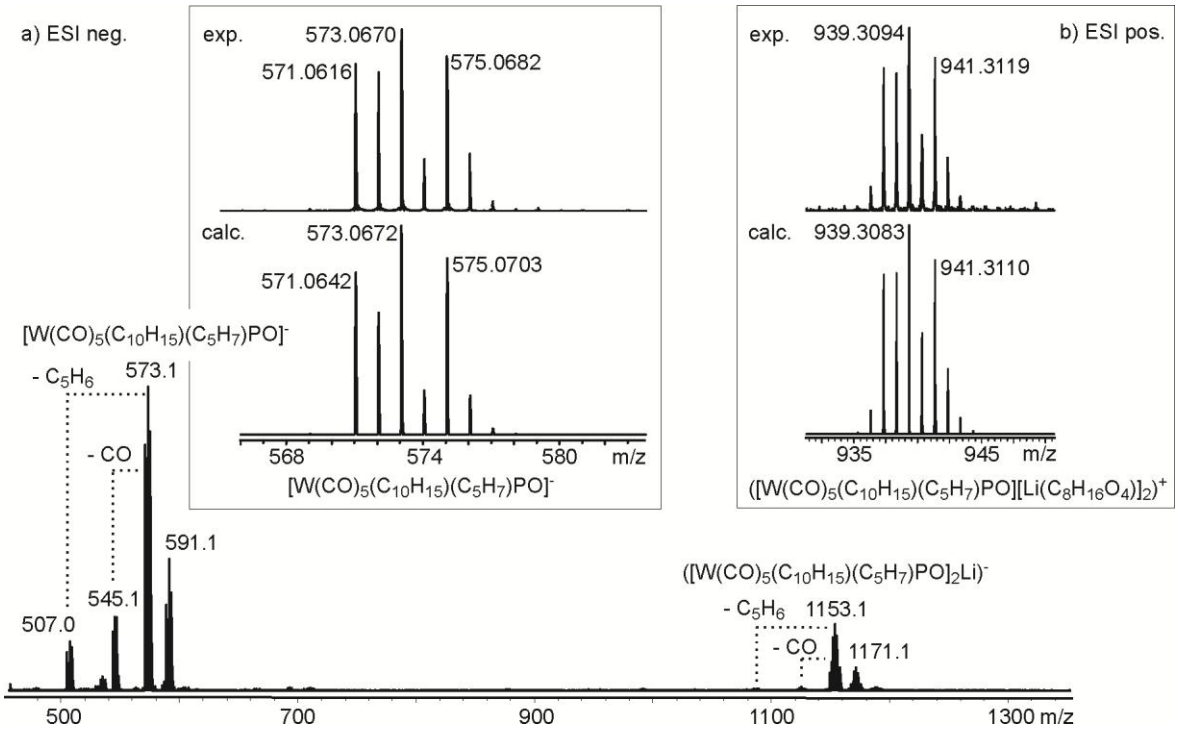

Figure S3: Positive and negative ESI-mass spectra of **14a**.

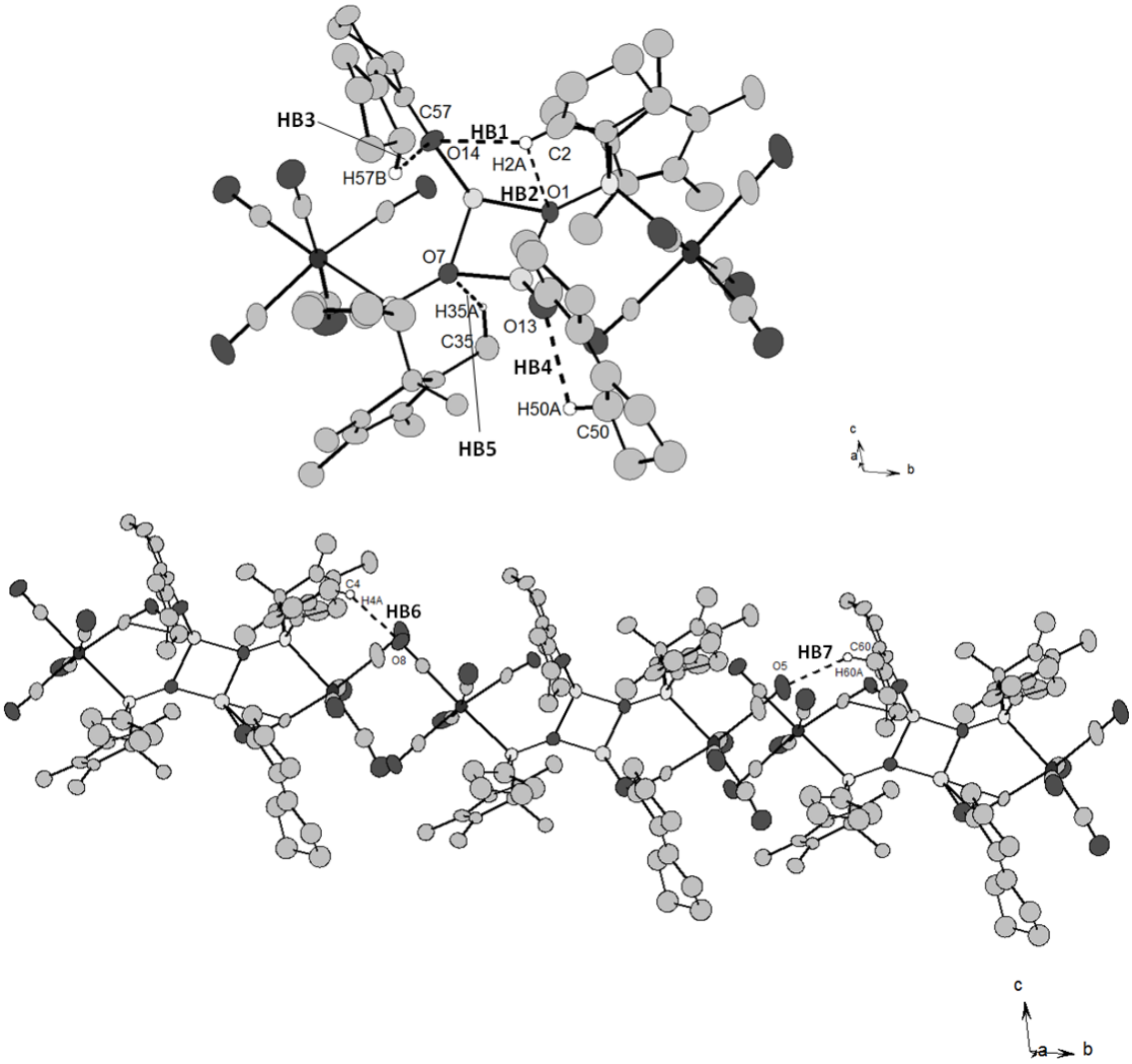

Figure S4: Intra- and intermolecular Hydrogen bonds (HB) in crystal of **15a**.

Table 1: Bond lengths (in Å) and angles of Hydrogen bonds (HB) in complex **15a**.

D–H···A	D···A	D–H	H···A	D–H···A
C2–H2A···O14 (HB1)	2.907(5)	0.95	2.58	100
C2–H2A···O1 (HB2)	2.940(14)	0.95	2.58	103
C57–H57B···O14 (HB3)	3.001(13)	0.99	2.58	106
C50–H50A–O13 (HB4)	2.901(12)	0.99	2.55	100
C35–H35A–O7 (HB5)	3.170(12)	0.98	2.51	124
C4–H4A–O8‘ (HB6)	3.186(14)	0.99	2.42	134
C60–H60A–O5‘ (HB7)	3.403(11)	0.99	2.53	146