Electronic Supplementary Information

"Synthesis and DFT Calculations of Spirooxaphosphirane Complexes"

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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**:

Complex 10b:

E = -2142.341133595 au (SCS-MP2/def2-TZVPPecp)

С	0.252416	-0.148158	0.077708	С	1.905712	4.249539	-3.085201
0	1.689218	-0.036091	0.160858	0	2.202004	5.027602	-3.867317
Ρ	0.959693	1.454369	-0.069195	С	0.859451	4.380816	-0.648977
С	-0.614019	-1.012946	0.899047	0	0.492625	5.256807	-0.015394
Н	-1.525596	-0.594789	1.310394	С	3.237906	3.070820	-1.079380
Н	-0.122457	-1.752498	1.520378	0	4.306649	3.151811	-0.689742
С	-0.515074	-1.194954	-0.622320	С	2.014073	1.523420	-2.925801
Н	-1.361560	-0.901914	-1.230525	0	2.346594	0.682299	-3.618516
Н	0.046355	-2.050161	-0.980471	С	-0.325134	2.802312	-2.452088
Н	0.835914	1.951397	1.252832	0	-1.397073	2.713868	-2.836934
Cr	1.453066	2.954024	-1.767651				

E = -2181.585348574 au (SCS-MP2/def2-TZVPPecp)

-0.069250	0.015322	0.164313	Н	1.751909	1.507745	1.070626
-0.053739	0.003231	1.616762	Cr	3.135485	-1.475489	1.310166
1.494309	0.115758	1.011956	С	4.487975	-2.799215	1.492169
-0.842279	1.039916	-0.660636	0	5.296949	-3.600985	1.579993
-0.317596	1.942968	-0.974802	С	4.442091	-0.183978	0.758341
-1.768312	1.317627	-0.150553	0	5.213518	0.590193	0.424849
-1.058966	-0.084226	-1.717382	С	3.332570	-0.927249	3.143945
-0.350730	-0.012752	-2.542106	0	3.438041	-0.609760	4.234957
-2.067132	-0.186359	-2.115873	С	1.781783	-2.721202	1.880945
-0.624666	-1.142387	-0.661007	0	0.974888	-3.450611	2.222931
0.065931	-1.924099	-0.974512	С	2.889000	-2.019470	-0.506943
-1.478732	-1.593218	-0.149577	0	2.732836	-2.340151	-1.592919
	-0.069250 -0.053739 1.494309 -0.842279 -0.317596 -1.768312 -1.058966 -0.350730 -2.067132 -0.624666 0.065931 -1.478732	-0.0692500.015322-0.0537390.0032311.4943090.115758-0.8422791.039916-0.3175961.942968-1.7683121.317627-1.058966-0.084226-0.350730-0.012752-2.067132-0.186359-0.624666-1.1423870.065931-1.924099-1.478732-1.593218	-0.0692500.0153220.164313-0.0537390.0032311.6167621.4943090.1157581.011956-0.8422791.039916-0.660636-0.3175961.942968-0.974802-1.7683121.317627-0.150553-1.058966-0.084226-1.717382-0.350730-0.012752-2.542106-2.067132-0.186359-2.115873-0.624666-1.142387-0.6610070.065931-1.924099-0.974512-1.478732-1.593218-0.149577	-0.0692500.0153220.164313H-0.0537390.0032311.616762Cr1.4943090.1157581.011956C-0.8422791.039916-0.660636O-0.3175961.942968-0.974802C-1.7683121.317627-0.150553O-1.058966-0.084226-1.717382C-0.350730-0.012752-2.542106O-2.067132-0.186359-2.115873C-0.624666-1.142387-0.661007O0.065931-1.924099-0.974512C-1.478732-1.593218-0.149577O	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

Com	plex	10c	•
Com	pien	IUU	•

E = -2220.842143914 au (SCS-MP2/def2-TZVPPecp)

С	0.054426	-0.013334	-0.076197	Н	-0.028989	2.091313	-0.718619
0	-0.065774	-0.218055	1.376430	Н	-1.449758	1.474800	0.124842
P	1.521913	0.003997	0.943132	С	-1.317341	0.754432	-1.926827
С	-0.676812	1.221428	-0.606479	Н	-0.608794	0.878149	-2.751040

Н	-2.217451	1.317997	-2.175935	0	5.338725	-3.552630	2.149156
С	-1.583771	-0.740362	-1.690544	С	4.497740	-0.235984	0.838138
Н	-1.763647	-1.294537	-2.612797	0	5.265430	0.542671	0.505713
Н	-2.456714	-0.866395	-1.044210	С	3.245471	-0.860558	3.170077
С	-0.317799	-1.207836	-0.951346	0	3.284548	-0.464586	4.240250
Н	0.481633	-1.401601	-1.671380	С	1.854105	-2.816852	1.902760
Н	-0.454699	-2.105696	-0.348229	0	1.068805	-3.584092	2.211102
Н	1.722151	1.384651	1.191394	С	3.133939	-2.176794	-0.419084
Cr	3.193825	-1.534426	1.382627	0	3.107713	-2.542186	-1.501283
С	4.542973	-2.791671	1.842968				

mplex 10d:		E = -2260.075062258 au (SCS-MP2/def2-TZVPPecp)				
-0.189487	-0.496298	-0.213985	С	0.100805	-1.304856	-1.458031
-0.463603	-1.278731	0.989683	Н	0.830208	-2.088398	-1.249287
1.001171	-0.497162	1.129851	Н	-0.830466	-1.799422	-1.759385
-1.154978	0.643162	-0.427168	Н	0.665988	0.673035	1.854555
-1.291853	1.201502	0.501224	Cr	2.905464	-1.769028	1.537044
-2.122370	0.193558	-0.686122	С	4.315276	-2.951797	1.978742
-0.684159	1.554333	-1.566353	0	5.144689	-3.681965	2.271580
0.230810	2.069801	-1.255417	С	3.433188	-1.695631	-0.304971
-1.438435	2.321824	-1.755138	0	3.755213	-1.634774	-1.399761
-0.406860	0.751650	-2.842461	С	4.063115	-0.279113	1.850778
-0.026361	1.413653	-3.624151	0	4.804409	0.573412	2.021747
-1.347959	0.324356	-3.208564	С	2.377257	-1.761040	3.382042
0.589699	-0.381764	-2.582108	0	2.076231	-1.748653	4.483501
1.556590	0.045865	-2.297006	С	1.821315	-3.299375	1.155261
0.752905	-0.967392	-3.489487	0	1.200426	-4.222640	0.907800
	mplex 10d: -0.189487 -0.463603 1.001171 -1.154978 -1.291853 -2.122370 -0.684159 0.230810 -1.438435 -0.406860 -0.026361 -1.347959 0.589699 1.556590 0.752905	mplex 10d: -0.189487 -0.496298 -0.463603 -1.278731 1.001171 -0.497162 -1.154978 0.643162 -1.291853 1.201502 -2.122370 0.193558 -0.684159 1.554333 0.230810 2.069801 -1.438435 2.321824 -0.406860 0.751650 -0.026361 1.413653 -1.347959 0.324356 0.589699 -0.381764 1.556590 0.045865 0.752905 -0.967392	$\begin{array}{llllllllllllllllllllllllllllllllllll$	$ \begin{array}{llllllllllllllllllllllllllllllllllll$	$ \begin{array}{llllllllllllllllllllllllllllllllllll$	mplex 10d: $E = -2260.075062258$ au (SCS-MP2/def2-T-0.189487-0.496298-0.213985C0.100805-1.304856-0.463603-1.2787310.989683H0.830208-2.0883981.001171-0.4971621.129851H-0.830466-1.799422-1.1549780.643162-0.427168H0.6659880.673035-1.2918531.2015020.501224Cr2.905464-1.769028-2.1223700.193558-0.686122C4.315276-2.951797-0.6841591.554333-1.566353O5.144689-3.6819650.2308102.069801-1.255417C3.433188-1.695631-1.4384352.321824-1.755138O3.755213-1.634774-0.4068600.751650-2.842461C4.063115-0.279113-0.0263611.413653-3.624151O4.8044090.573412-1.3479590.324356-3.208564C2.377257-1.7610400.589699-0.381764-2.582108O2.076231-1.7486531.5565900.045865-2.297006C1.821315-3.2993750.752905-0.967392-3.489487O1.200426-4.222640

Complex 11:

Complex 12c:

E = -2143.598288536 au (SCS-MP2/def2-TZVPPecp)

С	0.010293	0.014484	-0.006593	Cr	1.557866	2.965525	-1.687678
0	1.462349	0.022043	0.268775	С	2.058597	4.069723	-3.141663
Ρ	0.900762	1.566297	0.037882	0	2.368849	4.732442	-4.019138
С	-0.806026	-0.450239	1.170180	С	-0.193922	2.723123	-2.424618
Н	-0.451526	0.002622	2.097062	0	-1.255965	2.576937	-2.820080
Н	-0.726666	-1.538590	1.261981	С	0.914239	4.505348	-0.745260
Н	-1.857277	-0.186893	1.027565	0	0.524333	5.434693	-0.207469
С	-0.339656	-0.597569	-1.339517	С	3.302869	3.218178	-0.923972
Н	0.222462	-0.150057	-2.156318	0	4.354139	3.388553	-0.514157
Н	-0.110385	-1.667739	-1.314050	С	2.240979	1.426392	-2.610267
Н	-1.405806	-0.466329	-1.538995	0	2.667724	0.514686	-3.147058
Н	0.663657	2.022188	1.358714				

0

С

0 C

0

С

0

С

0

E = -1208.228138407 au (COSMO_{THF}/B3LYP-D3/def2-TZVPPecp)

1.732374

0.526987

0.135875

3.149230

4.212852

1.902763

2.274065

-0.709583

-1.778175

5.387219

4.675732

5.474990

3.495295

3.652241

1.718438

0.892694

2.940867

2.800541

-4.068543

-0.502362

0.219545

-1.080617

-0.686598

-3.053396

-3.752181 -2.486607

-2.872152

С	-0.093129	0.031708	0.039887
0	1.38/5/0	-0.044469	-0.082661
Ρ	0.885624	1.536588	0.048643
С	-0.799311	-0.354938	-1.235604
Н	-1.852625	-0.075181	-1.180366
Н	-0.356493	0.125497	-2.106436
Н	-0.736794	-1.438124	-1.371062
С	-0.642179	-0.619366	1.282479
Н	-0.608719	-1.705992	1.162636
Н	-1.684411	-0.326317	1.422074
Н	-0.083803	-0.361110	2.178885
С	1.257302	2.079000	1.743285
Н	2.281469	2.456166	1.757359
Н	1.155143	1.281713	2.474924
Н	0.586006	2.903206	1.992852
W	1.223393	3.217003	-1.790377
С	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.

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

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