

Influence of structural features of tri-functionalized aryl phosphates on the outcome of the $S_{RN}1$ process with stannyl anions. A DFT study.

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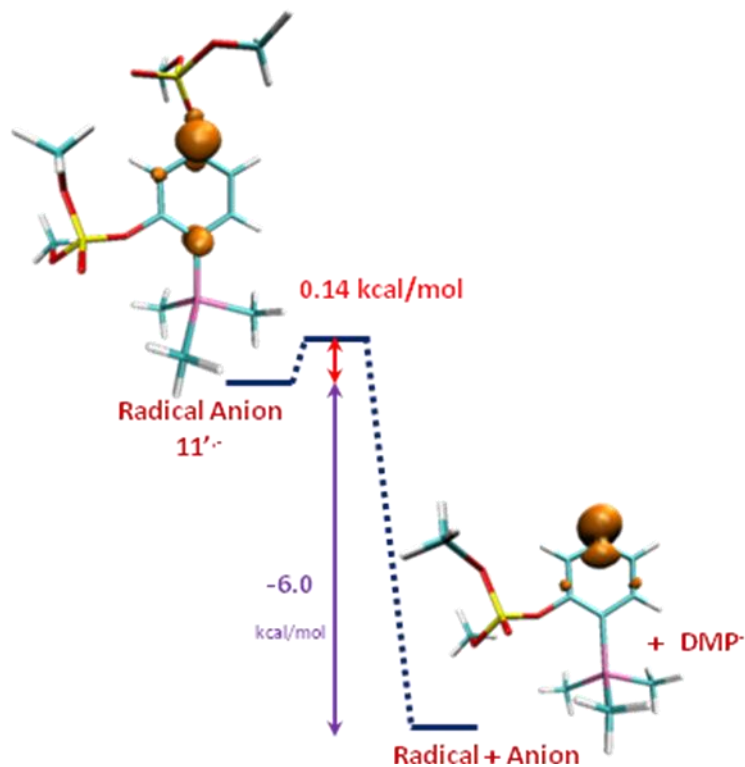
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PES for C-OP bond fragmentation of $11'^{\cdot-}$ (B3LYP/6-31+G* and LACVP (Sn))



Cartesians coordinates

$11'^{\cdot-}$

48

-1 2

scf done: -1797.940729 a.u. (B3LYP/6-31+G*/LACVP (Sn), PCM, solvent=methanol)

C	0.120043	-0.501964	-0.038033
C	0.080255	-0.361966	1.336980
C	1.258857	-0.223164	2.145057
C	2.463959	-0.159143	1.397679
C	2.555964	-0.258046	0.030037
C	1.374794	-0.581396	-0.723402
Sn	1.183501	-0.043912	4.238702
C	1.959144	-1.736209	5.340964
O	3.666036	0.072047	2.150097
P	4.898387	-0.960041	2.238913
O	4.680732	-2.245158	2.945947
O	1.337229	-0.043794	-2.118318
P	2.093175	-0.883763	-3.243371
O	1.202374	-2.175242	-3.619499
C	-0.225684	-2.088433	-3.712873
C	2.209780	1.705944	5.007851
C	-0.900047	0.159281	4.813062
O	5.986138	-0.021258	2.972641
C	6.326599	1.269873	2.446128

O	5.506727	-1.094414	0.750833
C	5.381555	-2.303367	-0.035542
O	1.811528	0.050703	-4.550253
C	2.450044	1.331014	-4.626728
O	3.519877	-1.243187	-3.035533
H	-0.806562	-0.606123	-0.600609
H	-0.894486	-0.385576	1.825493
H	-0.989808	0.257621	5.902750
H	-1.355841	1.044912	4.353807
H	-1.484075	-0.717284	4.505964
H	1.258415	-2.578541	5.285496
H	2.913375	-2.061455	4.913090
H	2.110078	-1.482831	6.398806
H	2.065006	1.801163	6.092225
H	3.285042	1.634419	4.808607
H	1.835526	2.618256	4.527952
H	3.511006	-0.163084	-0.471744
H	7.047115	1.701250	3.145638
H	6.783124	1.170591	1.455432
H	5.437678	1.904992	2.384614
H	6.364716	-2.489514	-0.476951
H	5.091501	-3.142183	0.602049
H	4.642873	-2.138653	-0.823295
H	-0.571743	-3.089728	-3.982247
H	-0.656544	-1.794371	-2.751710
H	-0.519530	-1.373326	-4.489457
H	2.182690	1.750826	-5.600602
H	2.090057	1.988249	-3.827174
H	3.538496	1.223934	-4.557056

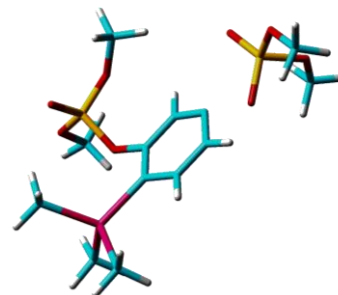
TS'

48

-1 2

scf done: -1797.931167 a.u. (B3LYP/6-31+G*/LACVP (Sn) , PCM,
solvent=methanol)

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.379771
C	1.244233	0.000000	2.072160
C	2.430396	0.174813	1.307132
C	2.372462	0.201709	-0.080839
C	1.153195	0.098071	-0.806445
O	1.223771	1.032563	3.400694
P	0.561080	0.452274	4.704590
O	1.609203	-0.550020	5.436360
C	3.003444	-0.235740	5.470232
Sn	1.083037	0.089556	-2.918756
C	0.597337	-1.830237	-3.778980
O	-1.256508	-0.068402	-0.690536
P	-2.283260	-1.307906	-0.599742
O	-1.837265	-2.608463	-1.154950
O	0.642278	1.719691	5.749124
C	-0.144295	2.877310	5.461409
O	-0.791260	-0.170283	4.629777
C	-0.303143	1.538715	-3.732218
C	3.051820	0.631237	-3.646888



O	-3.536873	-0.679343	-1.394210
C	-4.107606	0.578825	-1.000307
O	-2.829433	-1.357292	0.915423
C	-2.458370	-2.393993	1.854487
H	3.396410	0.236759	1.807322
H	3.311561	0.275433	-0.632414
H	3.059468	0.664389	-4.744000
H	3.354789	1.617541	-3.275323
H	3.809176	-0.095527	-3.328245
H	1.444383	-2.518935	-3.672106
H	-0.262285	-2.270189	-3.262537
H	0.362965	-1.736711	-4.847315
H	-0.209685	1.602065	-4.824094
H	-1.333359	1.256104	-3.489690
H	-0.115396	2.533847	-3.311753
H	-0.928818	-0.037212	1.936748
H	-4.928891	0.768395	-1.695777
H	-4.491041	0.520785	0.023645
H	-3.361805	1.376066	-1.074092
H	-3.388861	-2.807580	2.254067
H	-1.886517	-3.178014	1.352653
H	-1.871566	-1.940182	2.656342
H	3.493692	-1.070292	5.980115
H	3.403782	-0.135394	4.456471
H	3.179689	0.691313	6.029110
H	0.020697	3.579336	6.284473
H	0.170731	3.335867	4.516321
H	-1.209239	2.620442	5.407767

Radical'

35

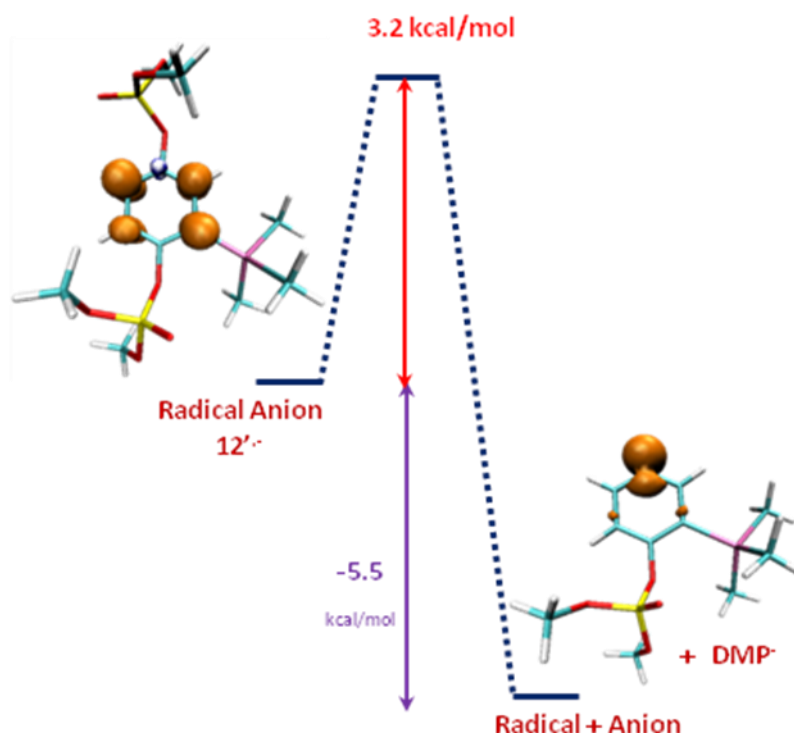
0 2

scf done: -1075.650583 a.u. (B3LYP/6-31+G*/LACVP(Sn), PCM, solvent=methanol)

C	-0.182778	-0.151996	0.172316
C	-0.138756	-0.028630	1.543249
C	1.144068	0.061881	2.115963
C	2.320659	0.019805	1.344948
C	2.161338	-0.114746	-0.039606
C	0.907296	-0.193602	-0.667235
Sn	4.258688	0.163710	2.307725
C	3.858728	0.996727	4.254191
O	3.314443	-0.080244	-0.849162
P	3.926005	-1.351589	-1.642843
O	2.821359	-1.582971	-2.799672
C	2.714101	-2.878614	-3.433296
C	5.137030	-1.781101	2.516861
C	5.547446	1.498286	1.222804
O	4.279200	-2.551900	-0.855553
O	5.189953	-0.670089	-2.350788
C	5.071612	0.515238	-3.164921
H	-1.032032	0.003084	2.161149
H	1.212471	0.170424	3.197283
H	4.799642	1.160477	4.792716
H	3.342866	1.960802	4.179259
H	3.242514	0.325794	4.863790

H	4.546296	-2.394799	3.206189
H	5.175270	-2.290174	1.548988
H	6.154559	-1.700969	2.916763
H	6.406316	1.783197	1.841597
H	5.923752	1.022813	0.311632
H	5.013524	2.412116	0.939668
H	0.832304	-0.279380	-1.746488
H	6.066972	0.695376	-3.573740
H	4.356449	0.352467	-3.977006
H	4.757422	1.363472	-2.550689
H	3.572651	-3.051518	-4.090134
H	2.658127	-3.666011	-2.678257
H	1.796258	-2.846511	-4.022423

PES for C-OP bond fragmentation of 12^{•-} (B3LYP/6-31+G* and LACVP (Sn))



Cartesians coordinates

12^{•-}

48

-1 2

scf done: -1797.939521 a.u. (B3LYP/6-31+G*/LACVP (Sn), PCM, solvent=methanol)

C	0.088623	0.082873	0.025120
C	0.086943	-0.026324	1.437950
C	1.390165	-0.114483	2.061492
C	2.541741	-0.143655	1.295668
C	2.551726	-0.068285	-0.131907

C	1.240719	0.074988	-0.777101
Sn	-1.693831	-0.056918	2.542811
C	-3.419153	0.283603	1.276296
Sn	4.432030	-0.387056	-1.028915
C	5.024517	1.050651	-2.554239
Sn	0.867097	0.455011	-2.831446
C	5.975683	-0.253492	0.490464
C	4.783036	-2.319966	-1.986135
C	-2.080085	-1.907607	3.629865
C	-1.749297	1.451909	4.112233
H	1.483477	-0.154826	3.148011
H	3.492254	-0.224240	1.828023
H	6.967699	-0.320624	0.024910
H	5.918307	0.696618	1.035030
H	5.891078	-1.066597	1.221465
H	4.687228	-3.127155	-1.249800
H	4.062977	-2.509859	-2.790045
H	5.794304	-2.362684	-2.414499
H	6.075771	0.883159	-2.825018
H	4.426937	0.966783	-3.468896
H	4.927957	2.076812	-2.180101
H	-0.889900	0.184572	-0.471045
H	-2.992322	-1.825445	4.236790
H	-2.201928	-2.747423	2.935397
H	-1.245567	-2.147735	4.300661
H	-4.341218	0.268818	1.871472
H	-3.355564	1.256043	0.773538
H	-3.503609	-0.488979	0.502963
H	-2.677552	1.382461	4.695007
H	-0.905654	1.327707	4.802790
H	-1.684163	2.459770	3.685134
C	-1.253188	0.271479	-3.244907
C	1.407577	2.444446	-3.530361
C	1.813244	-0.912550	-4.234217
H	-1.433204	0.377218	-4.322798
H	-1.637321	-0.706191	-2.930748
H	-1.835478	1.043668	-2.728819
H	1.341121	-0.804049	-5.219822
H	2.885622	-0.723261	-4.354605
H	1.686968	-1.952056	-3.909457
H	1.270959	2.529035	-4.616925
H	0.772790	3.195941	-3.045331
H	2.450767	2.683476	-3.296396

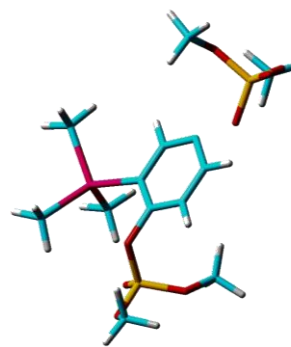
TS'

48

-1 2

scf done: -1797.934358 a.u. (B3LYP/6-31+G*/LACVP (Sn) , PCM,
solvent=methanol)

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.427437
C	1.184161	0.000000	2.179537
C	2.397266	-0.042399	1.467168
C	2.437876	-0.050638	0.061890
C	1.257538	-0.056922	-0.668682



Sn	1.017322	0.148716	4.315612
C	0.747393	-1.769837	5.259507
O	3.657295	0.007137	2.160982
P	4.396613	-1.344093	2.623250
O	3.887040	-2.002101	3.852177
O	-1.074324	-1.110631	-0.605841
P	-2.216350	-0.503131	-1.506576
O	-3.294058	-1.719875	-1.618746
C	-3.715160	-2.421578	-0.445916
C	2.642781	1.203189	5.261757
C	-0.780614	1.285425	4.726972
O	5.917729	-0.841919	2.772438
C	6.582239	-0.146574	1.705635
O	4.477899	-2.303621	1.324866
C	3.471302	-3.311593	1.084645
O	-3.066227	0.546853	-0.573957
C	-2.796055	1.950267	-0.672472
O	-1.894973	0.055492	-2.849222
H	1.289771	-0.056590	-1.756630
H	-0.962831	0.048974	1.936025
H	-1.669905	0.787843	4.322602
H	-0.921274	1.401562	5.809761
H	-0.725727	2.285020	4.280007
H	0.523847	-1.650489	6.327387
H	-0.082314	-2.315219	4.793992
H	1.662226	-2.359856	5.150858
H	3.535923	0.571888	5.293186
H	2.885466	2.117893	4.708924
H	2.373354	1.481650	6.288671
H	3.403272	-0.037364	-0.442813
H	7.569226	0.122189	2.089770
H	6.688190	-0.799210	0.832677
H	6.027176	0.755749	1.432883
H	3.238574	-3.840968	2.012908
H	2.571311	-2.847997	0.672654
H	3.906728	-4.000183	0.356581
H	-2.853387	-2.832158	0.091086
H	-4.280044	-1.757299	0.219249
H	-4.363531	-3.233761	-0.788695
H	-3.561877	2.452049	-0.072371
H	-1.800380	2.175820	-0.275768
H	-2.859892	2.281943	-1.714477

Radical'

35

0 2

scf done: -1075.650675 a.u. (B3LYP/6-31+G*/LACVP(Sn),PCM, solvent=methanol)

C	0.154425	0.026184	-0.144836
C	0.176737	-0.059955	1.252725
C	1.346973	-0.175234	2.007903
C	2.581687	-0.230940	1.342761
C	2.545752	-0.154173	-0.033184
C	1.407962	-0.023995	-0.801460
O	-1.050715	0.066532	1.941221
P	-1.816560	-1.148643	2.683873

O	-0.843229	-1.436891	3.942351
C	-0.885247	-2.726673	4.594017
Sn	-1.666624	0.243261	-1.312095
C	-1.007927	0.989626	-3.221831
C	-2.624992	-1.659204	-1.554581
C	-2.976582	1.681765	-0.400169
O	-2.176698	-2.336224	1.879997
O	-3.093273	-0.375755	3.265135
C	-2.972331	0.812540	4.074200
H	3.509507	-0.323570	1.900863
H	1.467409	0.044275	-1.885232
H	-1.872533	1.199499	-3.862551
H	-0.438169	1.919229	-3.111304
H	-0.377257	0.262462	-3.746064
H	-3.596077	-1.539022	-2.048833
H	-2.007290	-2.322619	-2.170119
H	-2.778186	-2.133784	-0.580695
H	-2.424767	2.581658	-0.107254
H	-3.763987	1.977812	-1.103086
H	-3.451826	1.262969	0.492150
H	1.290096	-0.220542	3.090928
H	-3.988435	1.071283	4.375781
H	-2.358408	0.613504	4.957960
H	-2.535168	1.624907	3.487252
H	-1.815466	-2.835763	5.160847
H	-0.803512	-3.527476	3.855501
H	-0.032235	-2.744708	5.274319

Cartesians coordinates

15⁻

48

-1 2

scf done: -1797.865219 a.u. (B3LYP/6-31+G*/LACVP (Sn))

C	0.169138	0.131466	-0.151126
C	0.049531	-0.087684	1.272275
C	1.294063	-0.254392	1.982434
C	2.497850	-0.174328	1.330680
C	2.640034	0.065017	-0.069813
C	1.402927	0.204037	-0.751168
H	1.306629	-0.474742	3.048396
O	3.681398	-0.300499	2.111111
P	4.744581	-1.505701	1.991452
O	4.263195	-2.899476	2.144265
O	1.401478	0.426679	-2.164691
P	2.344857	-0.340435	-3.218112
O	2.025787	-1.912605	-3.142532
C	0.682849	-2.405199	-2.962910
O	5.774245	-1.063353	3.154637
C	6.328681	0.258613	3.193140
O	5.626783	-1.229096	0.664201
C	5.496810	-2.043634	-0.522132
O	1.589603	0.075020	-4.598139

C	1.663208	1.436384	-5.041104
O	3.800119	-0.051673	-3.206631
H	-0.713817	0.216762	-0.783750
Sn	-1.784464	0.067297	2.272708
H	3.574346	0.405163	-0.500832
H	6.981129	0.288951	4.069838
H	6.913747	0.456208	2.288251
H	5.533602	1.004169	3.291498
H	6.470041	-2.008340	-1.018819
H	5.246594	-3.072332	-0.248882
H	4.728602	-1.624292	-1.175154
H	0.759019	-3.494159	-3.000476
H	0.290929	-2.091274	-1.992135
H	0.034745	-2.049092	-3.770672
H	1.188202	1.466156	-6.025196
H	1.123516	2.093011	-4.349528
H	2.707119	1.758212	-5.122636
C	-3.387188	-0.769597	1.066650
C	-1.727083	-1.004426	4.155094
C	-2.529271	2.060630	2.795564
H	-4.352032	-0.675736	1.581955
H	-3.470508	-0.251157	0.103076
H	-3.209025	-1.831806	0.860951
H	-2.728168	-1.050045	4.603074
H	-1.368230	-2.029846	4.010363
H	-1.060196	-0.512638	4.873691
H	-3.517729	1.997296	3.273850
H	-1.843506	2.561564	3.489957
H	-2.620599	2.690541	1.901994

Cartesians coordinates

5⁻

48

-1 2

scf done: -599.792721 a.u. (B3LYP/6-31+G*/LACVP (Sn))

C	0.088623	0.082873	0.025120
C	0.086943	-0.026324	1.437950
C	1.390165	-0.114483	2.061492
C	2.541741	-0.143655	1.295668
C	2.551726	-0.068285	-0.131907
C	1.240719	0.074988	-0.777101
Sn	-1.693831	-0.056918	2.542811
C	-3.419153	0.283603	1.276296
Sn	4.432030	-0.387056	-1.028915
C	5.024517	1.050651	-2.554239
Sn	0.867097	0.455011	-2.831446
C	5.975683	-0.253492	0.490464
C	4.783036	-2.319966	-1.986135
C	-2.080085	-1.907607	3.629865
C	-1.749297	1.451909	4.112233
H	1.483477	-0.154826	3.148011

H	3.492254	-0.224240	1.828023
H	6.967699	-0.320624	0.024910
H	5.918307	0.696618	1.035030
H	5.891078	-1.066597	1.221465
H	4.687228	-3.127155	-1.249800
H	4.062977	-2.509859	-2.790045
H	5.794304	-2.362684	-2.414499
H	6.075771	0.883159	-2.825018
H	4.426937	0.966783	-3.468896
H	4.927957	2.076812	-2.180101
H	-0.880099	0.184572	-0.471045
H	-2.992322	-1.825445	4.236790
H	-2.201928	-2.747423	2.935397
H	-1.245567	-2.147735	4.300661
H	-4.341218	0.268818	1.871472
H	-3.355564	1.256043	0.773538
H	-3.503609	-0.488979	0.502963
H	-2.677552	1.382461	4.695007
H	-0.905654	1.327707	4.802790
H	-1.684163	2.459770	3.685134
C	-1.253188	0.271479	-3.244907
C	1.407577	2.444446	-3.530361
C	1.813244	-0.912550	-4.234217
H	-1.433204	0.377218	-4.322798

Cartesians coordinates

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-1 2

scf done: -599.795110 a.u. (B3LYP/6-31+G*/LACVP (Sn))

C	-0.123332	0.186489	0.200483
C	-0.098189	0.042116	1.610468
C	1.091696	-0.021051	2.344266
C	2.327024	0.085829	1.637018
C	2.348752	0.125141	0.221902
C	1.136516	0.163478	-0.473469
Sn	1.064980	-0.271275	4.462290
C	1.677862	1.569894	5.430256
H	1.152907	0.182921	-1.566183
Sn	-1.948169	0.398285	-0.862215
C	-2.437192	-1.455206	-1.884235
C	-0.919642	-0.712014	5.206804
C	2.470774	-1.779299	5.138729
C	-3.610277	0.772290	0.476405
C	-1.881665	1.890885	-2.439708
H	3.267026	0.097200	2.193117
Sn	4.209866	0.097219	-0.834346
H	-1.048831	-0.021845	2.147116
H	2.440927	-1.875911	6.232451
H	2.239938	-2.757141	4.700246
H	3.495238	-1.511740	4.847851
H	-0.912444	-0.776152	6.303786
H	-1.632227	0.071094	4.916941
H	-1.288067	-1.664977	4.811122
H	1.788082	1.434140	6.513719

H	2.639039	1.913074	5.028229
H	0.940326	2.363201	5.256885
H	-4.557077	0.784583	-0.080579
H	-3.677433	-0.011145	1.243223
H	-3.503003	1.734951	0.988632
H	-3.336169	-1.346188	-2.504241
H	-1.610778	-1.768420	-2.534231
H	-2.615712	-2.259174	-1.159514
H	-2.850894	1.950424	-2.954294
H	-1.643538	2.882041	-2.037124
H	-1.115493	1.634798	-3.184027
C	3.903709	0.158051	-2.975479
C	5.404987	1.826964	-0.315467
C	5.397230	-1.643052	-0.324646
H	4.863280	0.082574	-3.504415
H	3.265416	-0.669229	-3.306800
H	3.422651	1.097192	-3.276976
H	6.350304	-1.641921	-0.869870
H	5.618236	-1.659591	0.750236
H	4.859737	-2.566098	-0.572276
H	6.414502	1.754453	-0.740709
H	4.939485	2.746678	-0.690441
H	5.496403	1.918867	0.773741