Supporting information

Table S1: Relative energy [ΔE_{rel} = E($R_3E{-}O{-}C{\equiv}P$)–E($R_3E{-}P{=}C{=}O$)] of the oxyphosphaalkynes ($Ph_3E{-}O{-}C{\equiv}P$) compared to that of the corresponding phosphaketenes ($Ph_3E{-}P{=}C{=}O$) using different functionals and the cc-pVDZ(-PP) basis set (E = C, Si, Ge, Sn).

Functional	E = C	E = Si	E = Ge	E = Sn	E = Pb
B3LYP	18.5	7.9	16.8	20.7	23.1
M06-2X	19.3	7.9	15.5	19.6	21.7
ωB97XD	20.8	10.8	18.9	22.8	24.5

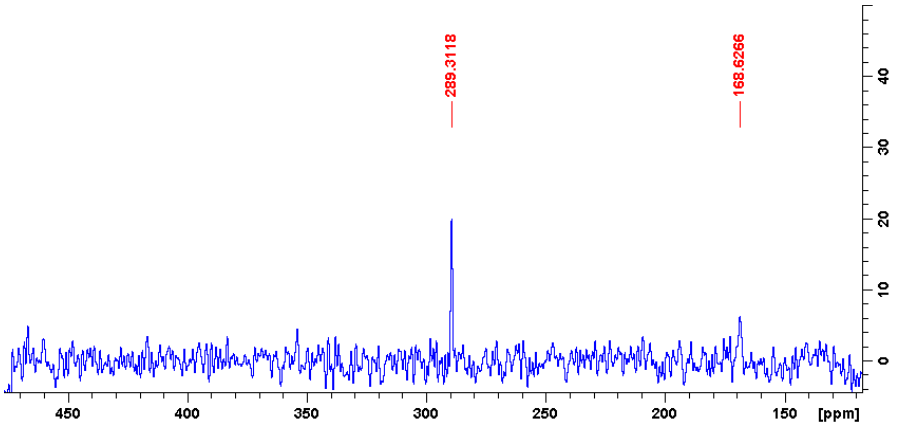

Figure S1: ^{17}O-NMR spectrum of $^{i}Pr_3Si{-}P{=}C{=}O$ (ns 307200, sw 365 ppm, O1P 300 ppm, D1 0.01 sec, aq 0.01 sec.) The excess of the $^{i}Pr_3SiOTf$ appears at 168.6 ppm.

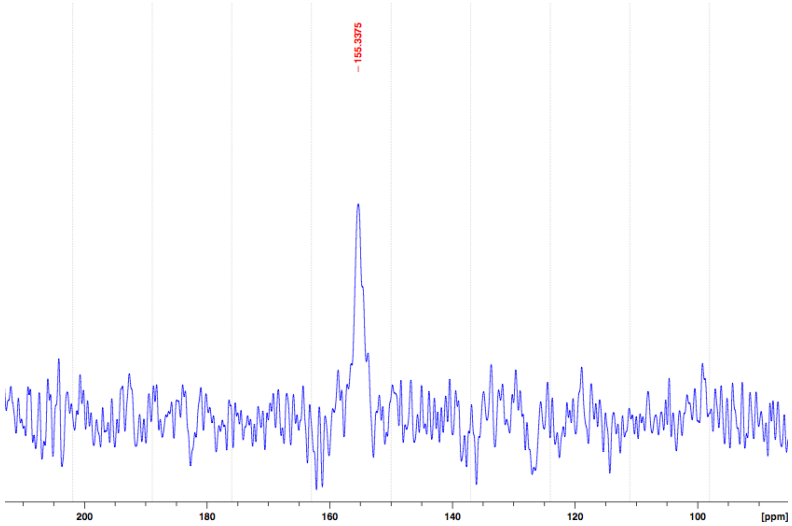

Figure S2: ^{17}O-NMR spectrum of Na(OCP) (ns 307200, sw 365 ppm, O1P 300 ppm, D1 0.01 sec, aq 0.01 sec.)

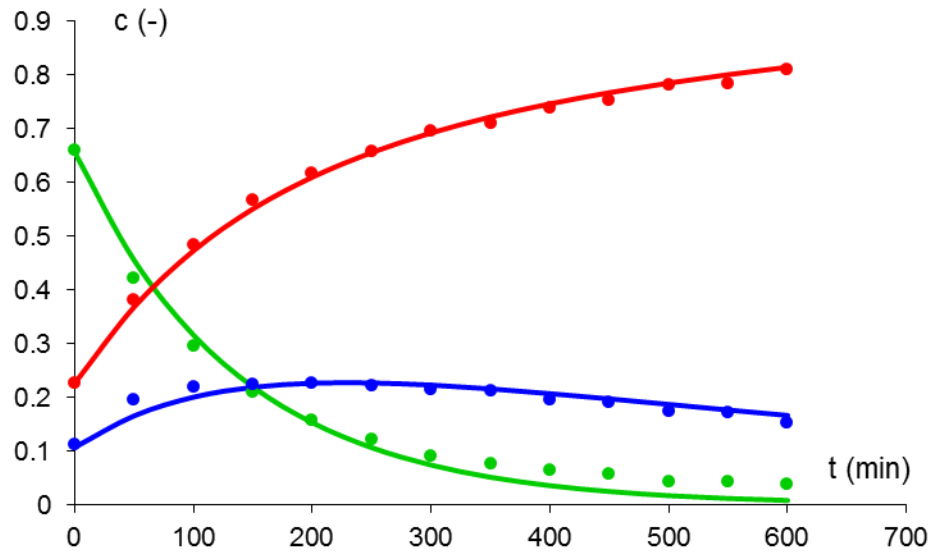

Figure S3: Fitted (lines) and measured (dots) relative concentrations vs. time (min) for the rearrangement of $^{i}Pr_3Si{-}OCP$ (green) to the two isomers of $^{i}Pr_3Si{-}PCO$ (blue and red). The nonlinear model was fitted using the Matlab program.

Total energies and Cartesian coordinates at the B3LYP/cc-pVDZ(-PP) level

$^{i}Pr_3SiOCP$
HF= −1099.839841

C	−0.095853	−0.030534	−0.570668
P	0.050030	−0.021840	0.996496
O	−0.163212	−0.042928	−1.851725
Si	−1.618199	−0.175178	−2.871656
C	−2.455450	1.538953	−2.852677
C	−1.501830	2.671356	−3.280199
C	−2.689496	−1.524077	−2.053920
C	−1.959860	−2.874117	−1.931658
C	−4.063633	−1.689694	−2.730721
C	−0.869832	−0.693940	−4.549200
C	0.519670	−0.097014	−4.839954
C	−1.844242	−0.436807	−5.716317
C	−3.118051	1.866499	−1.499429
H	−0.742018	−1.789316	−4.456364
H	−2.858447	−1.144856	−1.028249
H	−3.257556	1.465925	−3.614386
H	−3.617445	2.849772	−1.545877
H	−3.880088	1.124877	−1.212129
H	−2.375821	1.911468	−0.685758
H	−2.027122	3.642006	−3.272432
H	−0.644501	2.755157	−2.592183

H	−1.101387	2.522823	−4.295266
H	0.933709	−0.526954	−5.768694
H	0.475816	0.995642	−4.979905
H	1.231016	−0.297966	−4.025563
H	−1.439222	−0.846080	−6.657851
H	−2.831161	−0.901601	−5.556686
H	−2.008470	0.642291	−5.876750
H	−2.575511	−3.596179	−1.367854
H	−1.761965	−3.321390	−2.920857
H	−0.998258	−2.779145	−1.403645
H	−4.691813	−2.399991	−2.165592
H	−4.620242	−0.740699	−2.796712
H	−3.967969	−2.091501	−3.754033

$^{i}Pr_3SiPCO$

HF = −1099.850911

C	−0.056258	−0.105181	0.036114
Si	−0.001596	0.061888	1.958123
C	1.821639	0.056334	2.604824
C	−0.975643	1.623431	2.526627
P	−0.923080	−1.845880	2.944356
C	−2.214092	−1.886664	1.868746
O	−3.132805	−1.986862	1.156430
C	2.479135	1.445179	2.470936
C	2.022866	−0.500621	4.024952
H	2.342302	−0.628459	1.909229
C	0.361208	1.179590	−0.706297
C	0.740247	−1.314188	−0.485652
H	−1.123624	−0.285529	−0.193838
H	−0.388613	2.469929	2.117861
C	−2.388215	1.695492	1.921667
C	−1.031451	1.783549	4.055331
H	−2.886466	2.638575	2.207099
H	−2.380420	1.647782	0.821059
H	−3.024119	0.871385	2.286196
H	−1.564213	2.710383	4.332088
H	−1.567034	0.941709	4.525365
H	−0.028912	1.834149	4.508412
H	3.096645	−0.518382	4.282882
H	1.516810	0.114797	4.787189
H	1.647566	−1.531210	4.127838
H	3.552891	1.390261	2.722820
H	2.402944	1.856255	1.451872
H	2.023771	2.177985	3.158089
H	0.585971	−1.443634	−1.571162
H	1.824822	−1.181990	−0.328398

H	0.444218	−2.252033	0.009487
H	0.210735	1.062762	−1.794050
H	−0.216223	2.062787	−0.389362
H	1.429806	1.407715	−0.554959

^{i}PrNCP^{-}

HF = −552.764175

C	−0.021037	0.089100	0.293292
C	0.165502	0.101784	1.821372
N	1.573420	0.154156	2.186173
C	2.302256	−0.877675	2.051253
P	3.284524	−2.166538	1.910547
C	−0.553874	1.298112	2.456302
H	−0.305561	−0.829407	2.215862
H	−1.633708	1.305827	2.219472
H	−0.431362	1.277674	3.551738
H	−0.107372	2.240384	2.091888
H	−1.087137	0.017434	0.002844
H	0.401719	1.010146	−0.146843
H	0.520931	−0.769304	−0.135208

^{i}Pr(Me$_3$Si)NCP

HF = −962.033348

C	−0.537435	0.606919	0.263022
Si	0.141579	−0.002732	1.919316
N	1.964611	−0.137590	1.828817
C	2.500996	−1.351925	1.730582
P	3.176395	−2.773433	1.607414
C	−0.354339	1.178693	3.311465
C	−0.522188	−1.724868	2.287470
H	−1.456007	1.202181	3.378797
H	0.033448	0.835497	4.284230
H	−0.013240	2.212759	3.148231
H	−1.639824	0.550502	0.270875
H	−0.256270	1.649056	0.046632
H	−0.173385	−0.026599	−0.562499
H	−1.618537	−1.668854	2.401727
H	−0.294259	−2.431620	1.475257
H	−0.096487	−2.131560	3.218217
C	2.959056	0.988465	1.907046
C	3.314451	1.305530	3.362424
H	3.861107	0.594161	1.412784
C	2.504303	2.221579	1.125390
H	3.306308	2.976504	1.136918
H	2.286763	1.971339	0.076308
H	1.610357	2.691278	1.565718

H	4.135331	2.040594	3.404042
H	2.454445	1.727459	3.906259
H	3.643838	0.394806	3.885484

OCP^-
HF = −454.731700

C	0.000000	0.000000	0.154049
O	0.000000	0.000000	1.361457
P	0.000000	0.000000	−1.481919

Ph_3COPC
HF = −1187.737317

C	−0.486276	−0.481130	0.397152
C	−0.535980	−0.071930	1.739502
C	0.667277	0.295327	2.372008
C	1.879109	0.252158	1.679867
C	1.914019	−0.152051	0.342571
C	0.726869	−0.517648	−0.295515
C	−1.846365	−0.084232	2.527120
C	−3.081300	−0.321537	1.645478
C	−3.593633	−1.609318	1.426622
C	−4.696353	−1.801285	0.588356
C	−5.298277	−0.715023	−0.050360
C	−4.789939	0.569881	0.159189
C	−3.694749	0.765400	1.003383
C	−2.067474	1.123565	3.442270
C	−2.907519	1.001781	4.561549
C	−3.182892	2.106452	5.367783
C	−2.638940	3.357797	5.061169
C	−1.816671	3.492688	3.941433
C	−1.529879	2.383132	3.138708
O	−1.824067	−1.340254	3.408535
C	−0.959209	−1.499645	4.345480
P	0.031688	−1.804368	5.526102
H	0.658369	0.617227	3.412382
H	2.800671	0.538137	2.191629
H	2.862168	−0.180305	−0.199290
H	0.739668	−0.834333	−1.340788
H	−1.401769	−0.771504	−0.117210
H	−3.130923	−2.464749	1.915853
H	−5.084111	−2.811204	0.436012
H	−6.159532	−0.867338	−0.704700
H	−5.251703	1.430276	−0.330437
H	−3.318579	1.776309	1.164575
H	−0.883555	2.504751	2.268989
H	−1.388037	4.464868	3.687689

H	−2.856585	4.222339	5.692238
H	−3.829390	1.988178	6.240176
H	−3.346457	0.033596	4.803805

Ph_3CPCO
HF = −1187.766833

C	−0.634317	0.300843	0.443920
C	−0.589636	−0.168088	1.770159
C	0.658756	−0.554258	2.282606
C	1.817772	−0.476118	1.504939
C	1.756657	−0.010098	0.189975
C	0.522472	0.380344	−0.335458
C	−1.879461	−0.159819	2.622421
C	−3.092335	−0.483242	1.719163
C	−3.175213	−1.747605	1.104172
C	−4.228273	−2.069921	0.248999
C	−5.225502	−1.127849	−0.025737
C	−5.148134	0.134728	0.561991
C	−4.093974	0.454367	1.426684
C	−2.044974	1.159633	3.398276
C	−3.133594	1.337449	4.277963
C	−3.307533	2.527423	4.982102
C	−2.393674	3.577686	4.833088
C	−1.312045	3.417291	3.969104
C	−1.140348	2.222925	3.256967
P	−1.894623	−1.701813	3.889860
C	−1.113178	−0.964553	5.204174
O	−0.610702	−0.562714	6.172897
H	0.732191	−0.933340	3.301511
H	2.772679	−0.789605	1.933299
H	2.660763	0.044534	−0.420594
H	0.453638	0.747868	−1.362107
H	−1.585939	0.613105	0.012963
H	−2.395314	−2.491209	1.286840
H	−4.267194	−3.061289	−0.208224
H	−6.051688	−1.377254	−0.695198
H	−5.912299	0.886388	0.350208
H	−4.053736	1.450576	1.865716
H	−0.287218	2.127174	2.586571
H	−0.586905	4.224291	3.840389
H	−2.526055	4.508517	5.389018
H	−4.160773	2.633611	5.656220
H	−3.850615	0.526032	4.414455

Ph_3SiOPC
HF = −1439.214176

C	−0.213642	−0.394986	0.248720
C	−0.254468	−0.088219	1.623070
C	0.959962	0.205264	2.278626
C	2.171061	0.188483	1.582946
C	2.190778	−0.115515	0.217920
C	0.997339	−0.406335	−0.448998
Si	−1.878092	−0.105032	2.567033
C	−3.367911	−0.488045	1.489237
C	−3.746766	−1.815693	1.208866
C	−4.840781	−2.088500	0.383423
C	−5.573650	−1.038659	−0.179108
C	−5.212995	0.284992	0.089645
C	−4.121342	0.556198	0.919150
C	−2.115847	1.411002	3.651948
C	−2.998443	1.362355	4.750151
C	−3.223155	2.491564	5.539672
C	−2.573517	3.694481	5.242206
C	−1.696562	3.762905	4.156538
C	−1.467765	2.629076	3.370422
O	−1.878529	−1.509962	3.644019
C	−1.024291	−1.771869	4.569902
P	−0.014699	−2.139844	5.716601
H	0.962064	0.441139	3.345401
H	3.102545	0.411735	2.108291
H	3.138375	−0.126243	−0.326123
H	1.009039	−0.644521	−1.515226
H	−1.138945	−0.628240	−0.283853
H	−3.187477	−2.643561	1.650673
H	−5.124049	−3.124179	0.181168
H	−6.429605	−1.252578	−0.823714
H	−5.786827	1.108351	−0.342221
H	−3.860383	1.596611	1.132251
H	−0.771288	2.693974	2.530607
H	−1.184732	4.699488	3.922961
H	−2.749693	4.578315	5.860035
H	−3.905356	2.433398	6.390970
H	−3.510677	0.428660	4.996121

Ph_3SiPCO
HF = −1439.226806

C	−0.217517	−0.583857	0.374291
C	−0.293356	−0.207479	1.729225
C	0.898096	0.190029	2.371229
C	2.116275	0.205199	1.687562
C	2.170151	−0.175549	0.342988
C	1.000323	−0.568498	−0.312471

Si	−1.936647	−0.248455	2.676258
C	−3.404756	−0.506820	1.497722
C	−3.644859	−1.752560	0.883011
C	−4.714197	−1.928757	0.000725
C	−5.571106	−0.860516	−0.282379
C	−5.353209	0.381044	0.320752
C	−4.281785	0.554720	1.202544
C	−2.152665	1.350163	3.676403
C	−2.911451	1.383624	4.862763
C	−3.112990	2.579028	5.557468
C	−2.556132	3.769775	5.080597
C	−1.798996	3.758826	3.905951
C	−1.600027	2.561027	3.211928
P	−2.121420	−2.118160	4.048657
C	−0.624682	−1.832395	4.767214
O	0.399914	−1.698336	5.303842
H	0.878971	0.498314	3.419614
H	3.026114	0.516425	2.206465
H	3.122333	−0.163156	−0.192853
H	1.033832	−0.862426	−1.364431
H	−1.122147	−0.888894	−0.156633
H	−2.991730	−2.602886	1.099343
H	−4.881296	−2.903885	−0.463168
H	−6.410005	−0.997687	−0.968926
H	−6.021975	1.218581	0.107706
H	−4.130542	1.530319	1.670593
H	−1.000015	2.571087	2.298384
H	−1.358169	4.684884	3.528771
H	−2.709218	4.704222	5.625946
H	−3.702762	2.579997	6.477381
H	−3.342679	0.459056	5.254857

Ph_3GeOPC
HF = −3226.697151

C	−0.157677	0.151410	0.113327
C	−0.149340	−0.024856	1.508791
C	1.077316	−0.236043	2.161641
C	2.271222	−0.275038	1.433711
C	2.250838	−0.096888	0.047942
C	1.035797	0.118730	−0.611299
Ge	−1.829556	−0.019935	2.503826
O	−2.845292	1.423822	1.775817
C	−2.483758	2.648588	1.852274
P	−2.079827	4.171263	1.915168
C	−3.038991	−1.486785	2.060926
C	−4.430526	−1.287048	2.032488

C	−5.290385	−2.347161	1.731393
C	−4.771109	−3.616969	1.459468
C	−3.389052	−3.825718	1.482923
C	−2.527286	−2.765235	1.779252
C	−1.635097	0.335436	4.412332
C	−0.833437	1.399032	4.868324
C	−0.712897	1.655350	6.236909
C	−1.384122	0.851123	7.163349
C	−2.182009	−0.208310	6.721205
C	−2.309791	−0.463082	5.352714
H	−0.310788	2.039610	4.154739
H	−0.094537	2.487927	6.580108
H	−1.286397	1.052049	8.232891
H	−2.708913	−0.836735	7.443072
H	−2.940718	−1.289997	5.017103
H	−4.842865	−0.295246	2.230395
H	−6.369763	−2.179835	1.705929
H	−5.444896	−4.444216	1.224045
H	−2.979612	−4.814805	1.264420
H	−1.447500	−2.938122	1.780179
H	1.107435	−0.366960	3.246349
H	3.218737	−0.439780	1.952073
H	3.183563	−0.122547	−0.520432
H	1.018125	0.264183	−1.693862
H	−1.099991	0.326137	−0.411786

Ph_3GePCO
HF = −3226.723846

C	−0.142654	−0.215537	0.110616
C	−0.150327	0.006317	1.499722
C	1.076558	0.207580	2.155550
C	2.279346	0.183613	1.443690
C	2.273336	−0.039632	0.063192
C	1.060768	−0.238749	−0.602710
Ge	−1.853803	−0.031613	2.495494
C	−2.207797	−1.838539	3.210128
C	−3.189123	−2.052901	4.194850
C	−3.444515	−3.338465	4.681939
C	−2.717994	−4.429237	4.194297
C	−1.736143	−4.229588	3.219927
C	−1.482147	−2.943310	2.732112
C	−3.331133	0.573162	1.336494
C	−4.539719	−0.141936	1.276403
C	−5.588421	0.293996	0.460065
C	−5.444192	1.452567	−0.308176
C	−4.246833	2.173213	−0.259376

C	−3.198730	1.736871	0.556096
P	−1.678510	1.256023	4.510568
C	−1.711195	2.700303	3.644597
O	−1.731092	3.734929	3.108982
H	1.093567	0.396065	3.232078
H	3.224334	0.344221	1.968441
H	3.213285	−0.054575	−0.493767
H	1.049191	−0.409928	−1.681969
H	−1.083348	−0.365418	−0.425699
H	−3.758746	−1.209402	4.595108
H	−4.210029	−3.487377	5.447380
H	−2.914594	−5.433574	4.577001
H	−1.161919	−5.077648	2.838792
H	−0.706760	−2.801861	1.975127
H	−2.269968	2.312377	0.577447
H	−4.127054	3.079214	−0.858379
H	−6.263374	1.793497	−0.945777
H	−6.520446	−0.275394	0.423618
H	−4.666166	−1.051976	1.867691

Ph_3SnOPC
HF = −1364.020351

C	0.029316	−0.470504	0.071677
C	0.030073	−0.045332	1.411543
C	1.234461	0.382862	1.995413
C	2.417036	0.390107	1.249095
C	2.406313	−0.031070	−0.083772
C	1.213004	−0.461982	−0.671948
Sn	−1.793903	−0.062063	2.545362
O	−2.920264	1.591281	1.851315
C	−2.523703	2.796437	1.944667
P	−2.062262	4.306412	2.038033
C	−3.209682	−1.575510	1.977056
C	−4.542141	−1.215222	1.711220
C	−5.475646	−2.191182	1.347940
C	−5.089963	−3.531631	1.249135
C	−3.766230	−3.898024	1.508986
C	−2.828601	−2.924319	1.869639
C	−1.564405	0.304433	4.651448
C	−0.987507	1.498647	5.121209
C	−0.841850	1.714720	6.495464
C	−1.262676	0.743918	7.409302
C	−1.839579	−0.443814	6.950314
C	−1.993667	−0.661958	5.577462
H	−0.670557	2.276996	4.423121
H	−0.400893	2.648713	6.851525

H	−1.145575	0.915571	8.481909
H	−2.176118	−1.201642	7.661884
H	−2.457886	−1.591305	5.235690
H	−4.850095	−0.169102	1.775335
H	−6.508321	−1.901368	1.139604
H	−5.821588	−4.291878	0.965610
H	−3.459847	−4.943718	1.427885
H	−1.795194	−3.229503	2.058416
H	1.259007	0.712678	3.037142
H	3.348287	0.727262	1.710301
H	3.330548	−0.023577	−0.666291
H	1.202808	−0.791650	−1.713536
H	−0.895798	−0.810332	−0.401451

Ph_3SnPCO
HF = −1364.053266

C	0.019892	−0.236050	0.043393
C	0.029928	0.018338	1.426297
C	1.259853	0.259201	2.061429
C	2.453221	0.239834	1.332064
C	2.431701	−0.019091	−0.041934
C	1.214051	−0.256084	−0.686053
Sn	−1.831355	−0.002459	2.540596
C	−2.249336	−1.979608	3.327869
C	−3.275539	−2.186136	4.266577
C	−3.544618	−3.467895	4.758281
C	−2.788842	−4.559555	4.319892
C	−1.763369	−4.366311	3.390013
C	−1.494632	−3.084304	2.897428
C	−3.457920	0.668899	1.273612
C	−4.620447	−0.109636	1.139488
C	−5.671321	0.314297	0.318510
C	−5.574052	1.523185	−0.376185
C	−4.423129	2.307137	−0.249750
C	−3.371514	1.883200	0.569036
P	−1.579179	1.413609	4.684712
C	−1.643849	2.812158	3.751041
O	−1.682715	3.821563	3.166592
H	1.291821	0.474925	3.132957
H	3.402669	0.430612	1.838591
H	3.364067	−0.032041	−0.611529
H	1.191172	−0.453843	−1.760689
H	−0.924046	−0.413275	−0.480048
H	−3.872498	−1.344204	4.628880
H	−4.345107	−3.612889	5.488066
H	−2.997443	−5.560312	4.705598

H	−1.167221	−5.215670	3.047017
H	−0.685008	−2.951066	2.174522
H	−2.482215	2.512980	0.653671
H	−4.342210	3.253569	−0.790075
H	−6.395116	1.855074	−1.016163
H	−6.568366	−0.302622	0.222567
H	−4.713675	−1.058238	1.675274

Ph_3PbOPC
HF = −1342.540184

C	0.155172	−0.723868	0.127318
C	0.141435	−0.093704	1.379215
C	1.272247	0.595828	1.837433
C	2.418793	0.651915	1.037469
C	2.436247	0.021406	−0.210183
C	1.306823	−0.665884	−0.664979
Pb	−1.708334	−0.195569	2.631861
O	−2.875826	1.623045	1.965005
C	−2.362846	2.775475	1.980504
P	−1.739015	4.236282	1.988392
C	−3.262528	−1.663373	1.958468
C	−4.529578	−1.180128	1.603594
C	−5.517194	−2.077907	1.182365
C	−5.243704	−3.447658	1.115847
C	−3.978300	−3.926241	1.466898
C	−2.983354	−3.035410	1.887827
C	−1.523925	0.244142	4.822209
C	−1.214288	1.541552	5.255503
C	−1.106439	1.798548	6.627559
C	−1.300930	0.772472	7.556872
C	−1.613384	−0.518000	7.119588
C	−1.729342	−0.785331	5.750638
H	−1.078013	2.357684	4.541740
H	−0.872180	2.810214	6.967151
H	−1.214145	0.979987	8.625933
H	−1.774083	−1.320427	7.843682
H	−1.989219	−1.796002	5.424394
H	−4.744235	−0.110170	1.644778
H	−6.504443	−1.701689	0.903699
H	−6.018315	−4.144178	0.786870
H	−3.760145	−4.995570	1.412071
H	−1.996622	−3.426104	2.151493
H	1.270741	1.094108	2.809361
H	3.299023	1.193887	1.391048
H	3.333096	0.068222	−0.832122
H	1.318434	−1.156351	−1.641260

H	−0.724719	−1.257850	−0.240537

Ph_3PbPCO
HF = −1342.576951

C	0.121726	−0.316588	0.013808
C	0.126606	0.008804	1.378142
C	1.336387	0.320896	2.012891
C	2.533827	0.300831	1.288325
C	2.527456	−0.028970	−0.070492
C	1.321811	−0.336357	−0.707567
Pb	−1.817029	0.002453	2.532464
C	−2.268016	−2.049246	3.361822
C	−3.305445	−2.239538	4.286426
C	−3.579332	−3.519855	4.781973
C	−2.818320	−4.613846	4.358928
C	−1.781371	−4.427446	3.440316
C	−1.504802	−3.148323	2.942352
C	−3.524872	0.721114	1.241078
C	−4.657841	−0.089259	1.079786
C	−5.717041	0.337171	0.269367
C	−5.650498	1.573900	−0.378480
C	−4.523634	2.385622	−0.216592
C	−3.461487	1.962752	0.590753
P	−1.493449	1.485867	4.738046
C	−1.650726	2.868634	3.794462
O	−1.752664	3.869908	3.200494
H	1.352081	0.591558	3.072068
H	3.474173	0.546585	1.788244
H	3.462983	−0.042422	−0.634720
H	1.311537	−0.589399	−1.770827
H	−0.813938	−0.549682	−0.502291
H	−3.905175	−1.393916	4.633966
H	−4.388848	−3.660629	5.502684
H	−3.032006	−5.612170	4.747951
H	−1.181503	−5.279213	3.109781
H	−0.686663	−3.017841	2.228607
H	−2.591932	2.613532	0.708123
H	−4.468462	3.354381	−0.719421
H	−6.478259	1.906535	−1.009254
H	−6.596300	−0.300326	0.146411
H	−4.725319	−1.058227	1.581923