Attractive PH$\cdots$HP interactions revealed by state-of-the-art *ab initio* calculations

Supporting Information

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Abstract

We report in this work a combined structural and state-of-the-art computational study of homopolar P-H$\cdots$H-P intermolecular contacts. Databases surveys have shown the abundance of such surprisingly unexplored contacts, which are usually accompanied by other weak interactions in the solid state. By means of a detailed theoretical study utilizing SAPT(DFT), MP2, SCS-MP2, MP2C and CCSD(T) methods and both aug-cc-pVXZ and aug-cc-pCVXZ (X = D, T, Q, 5) basis sets as well as extrapolation to the CBS limit, we have shown that P-H$\cdots$H-P contacts are indeed attractive and considerably strong. SAPT(DFT) calculations have revealed the dispersive nature of the P-H$\cdots$H-P interaction with only minor contribution of the inductive term, whereas the first-order electrostatic term is clearly overbalanced by the first-order exchange energy. In general the computed interaction energies follow the trend: $E_{\rm int}^{\rm MP2C} \approx E_{\rm int}^{\rm SCS-MP2} < E_{\rm int}^{\rm SAPT(DFT)} < E_{\rm int}^{\rm MP2}$. Our results have also shown that the aug-cc-pVDZ (or aug-cc-pCVDZ) basis set is not yet well-balanced and that the second-order dispersion energy term is the slowest converging among all SAPT(DFT) energy components. Comparing to aug-cc-pVXZ basis sets, their core-correlation counterparts have a modest influence on all supermolecular interaction energies and a negligible influence on both the SAPT(DFT) interaction energy and its components.

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Figure S1: P-H$\cdots$P (green) and P-H$\cdots$H-P (red) short contacts in the crystal structure of tetraphosphanylsilane (ICSD Refcode 408432). d1 = 2.97, d2 = 3.05, d3 = 3.19, d4 = 3.12, d5 = 2.52, d6 = 2.55, d7 = 2.12Å.

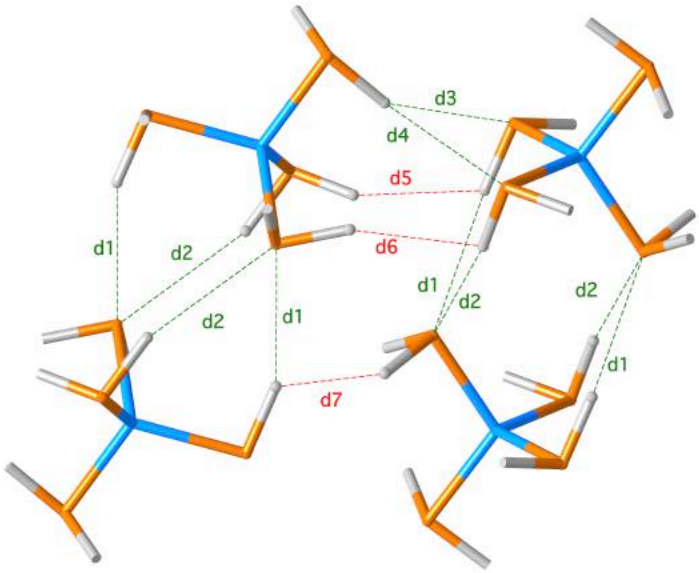

Figure S2: Calculated intermolecular H$\cdots$H distances as a function of the dissociation energy with (blue line) and without (red line) correction of the BSSE for dimers of PH_3, PH_2CH_3 and $PH(CH_3)_2$ with topology 1:1 (MP2/aug-cc-pVTZ).

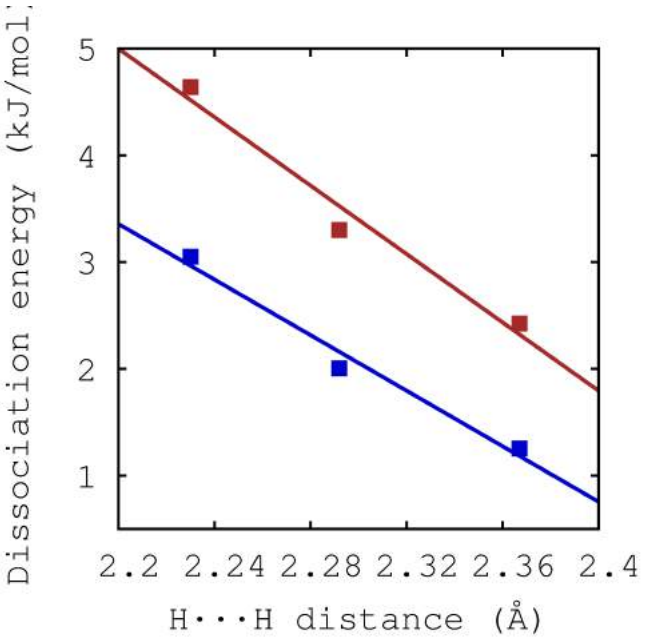

Figure S3: Values (in kJ/mol) of SAPT(DFT) energy components obtained by means of aug-cc-pCVXZ (X = D (1), T (2), Q (3), 5 (4)) basis sets and in the complete basis set limit (5) for dimers of DUCBUA and PH_3.

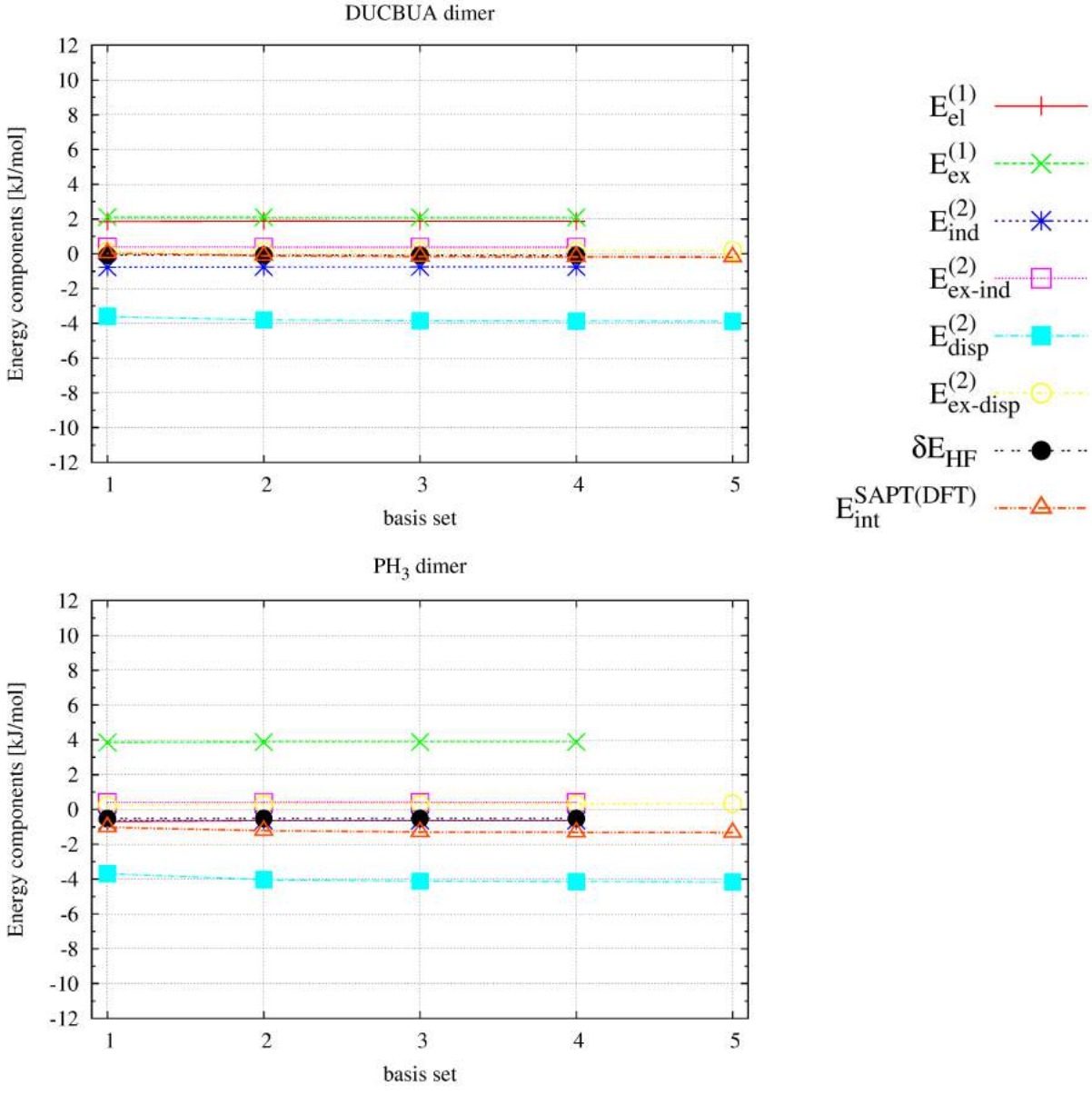

Figure S4: Dependences between components of the SAPT/CBS-based interaction energy and the P-H$\cdots$H angle in the PH_3 dimer The H$\cdots$H distance was fixed at the optimized (MP2/aug-cc-pVTZ) value at 180° (2.367Å) and the two P-H units involved in the interaction were kept parallel to each other for all angles.

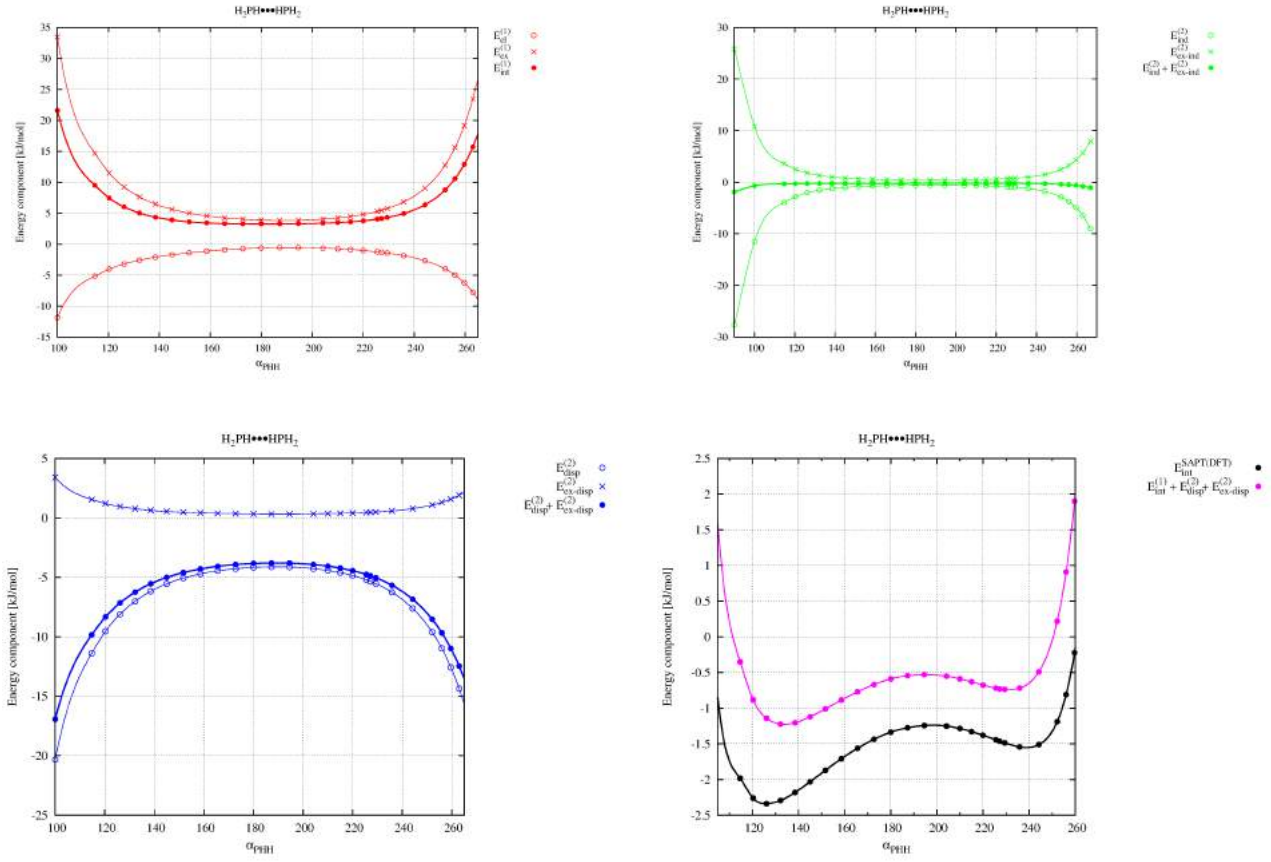

Figure S5: Dependence of the interaction energy on the electron density and DI(H,H).

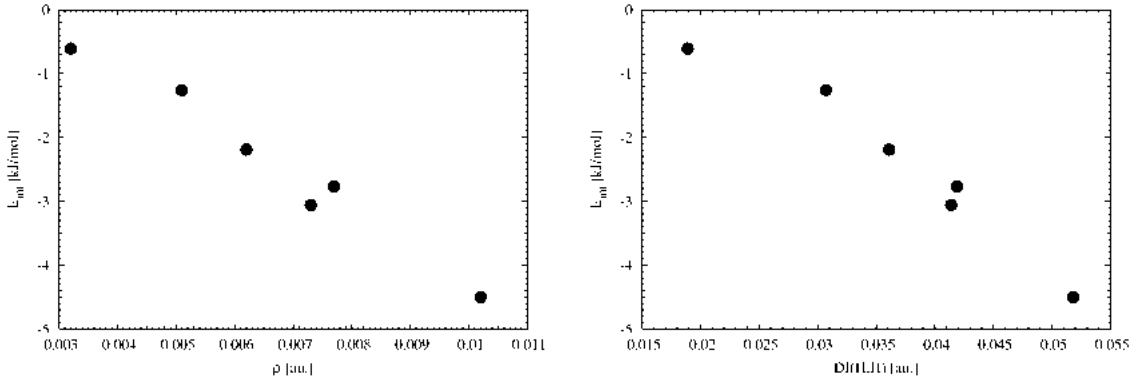

Table S1: SAPT(DFT)-based interaction energy components and interaction energies themselves (in kJ/mol) obtained by means of MP2, SCS-MP2, MP2C, and CCSD(T) methods and the aug-cc-pVXZ (X = D, T, Q, 5) basis sets and the CBS limit (X = 5).

Dimer	$E_{el}^{(1)}$	$E_{ex}^{(1)}$	$E_{ind}^{(2)}$	$E_{ex-ind}^{(2)}$	$E_{disp}^{(2)}$	$E_{ex-disp}^{(2)}$	δE_{HF}	$E_{int}^{SAPT(DFT)}$	E_{int}^{MP2}	$E_{int}^{SCS-MP2}$	E_{int}^{MP2C}	$E_{int}^{CCSD(T)}$
						aug-cc-pVDZ						
DUCBUA	1.844	2.105	-0.774	0.390	-3.598	0.150	-0.091	0.026	-0.527	0.341	0.027	
PH_3	-0.679	3.847	-0.628	0.408	-3.684	0.255	-0.531	-1.013	-1.011	-0.229	-0.369	-1.030
$PMeH_2$	-1.623	5.321	-0.882	0.632	-4.975	0.377	-0.727	-1.879	-1.890	-0.810	-1.035	-1.851
PMe_2H	-2.452	7.069	-1.246	0.954	-6.505	0.526	-0.941	-2.596	-2.729	-1.298	-1.572	-2.578
P_3H_5-T	-1.068	7.434	-1.560	1.058	-6.846	0.467	-1.036	-1.551	-2.359	-0.792	-0.766	-2.038
P_3H_5-C	-1.746	10.945	-2.576	1.770	-9.731	0.661	-1.625	-2.303	-3.870	-1.423	-1.014	-2.778
						aug-cc-pVTZ						
DUCBUA	1.876	2.103	-0.765	0.382	-3.793	0.169	-0.088	-0.116	-0.614	0.282	-0.131	
PH_3	-0.622	3.872	-0.641	0.415	-4.028	0.304	-0.528	-1.228	-1.258	-0.450	-0.688	-1.244
$PMeH_2$	-1.577	5.352	-0.904	0.650	-5.396	0.444	-0.724	-2.155	-2.185	-1.080	-1.427	-2.137
PMe_2H	-2.415	7.111	-1.292	1.003	-7.011	0.611	-0.937	-2.929	-3.064	-1.609	-2.034	-2.926
P_3H_5-T	-0.992	7.468	-1.593	1.086	-7.423	0.548	-1.032	-1.939	-2.768	-1.151	-1.301	-2.387
P_3H_5-C	-1.640	10.995	-2.621	1.809	-10.556	0.775	-1.619	-2.859	-4.496	-1.968	-1.795	-3.349
						aug-cc-pVQZ						
DUCBUA	1.876	2.102	-0.758	0.378	-3.840	0.177	-0.088	-0.153	-0.616	0.279	-0.154	
PH_3	-0.635	3.876	-0.635	0.411	-4.110	0.321	-0.528	-1.301	-1.323	-0.514	-0.773	
$PMeH_2$	-1.578	5.358	-0.901	0.649	-5.493	0.465	-0.722	-2.223	-2.261	-1.158	-1.535	
PMe_2H	-2.410	7.120	-1.294	1.008	-7.124	0.639	-0.934	-2.997	-3.147	-1.700	-2.164	
P_3H_5-T	-1.018	7.478	-1.589	1.086	-7.556	0.575	-1.031	-2.056	-2.860	-1.241	-1.426	
P_3H_5-C	-1.665	11.019	-2.616	1.811	-10.748	0.811	-1.616	-3.003	-4.635	-2.108	-1.978	
						aug-cc-pV5Z						
DUCBUA	1.874	2.102	-0.755	0.378	-3.851	0.180	-0.088	-0.160	-0.629	0.278	-0.157	
PH_3	-0.637	3.881	-0.634	0.412	-4.133	0.327	-0.526	-1.309	-1.338	-0.531	-0.796	
$PMeH_2$	-1.576	5.366	-0.900	0.651	-5.521	0.474	-0.720	-2.227	-2.279	-1.180	-1.559	
PMe_2H	-2.406	7.131	-1.294	1.010	-7.159	0.649	-0.931	-3.000	-3.168	-1.726	-2.187	
P_3H_5-T	-1.027	7.488	-1.588	1.089	-7.599	0.585	-1.028	-2.080	-2.883	-1.268	-1.472	
P_3H_5-C	-1.674	11.042	-2.617	1.817	-10.811	0.826	-1.611	-3.029	-4.671	-2.150	-2.044	
						aug-cc-pV5Z $\longrightarrow$ CBS limit						
DUCBUA	1.874	2.102	-0.755	0.378	-3.862	0.183	-0.088	-0.168	-0.647	0.276	-0.182	
PH_3	-0.637	3.881	-0.634	0.412	-4.157	0.333	-0.526	-1.328	-1.350	-0.546	-0.816	
$PMeH_2$	-1.576	5.366	-0.900	0.651	-5.550	0.483	-0.720	-2.246	-2.299	-1.205	-1.586	
PMe_2H	-2.406	7.131	-1.294	1.010	-7.196	0.659	-0.931	-3.027	-3.194	-1.758	-2.216	
P_3H_5-T	-1.027	7.488	-1.588	1.089	-7.644	0.595	-1.028	-2.115	-2.899	-1.288	-1.511	
P_3H_5-C	-1.674	11.042	-2.617	1.817	-10.877	0.842	-1.611	-3.078	-4.708	-2.194	-2.114	

Table S2: SAPT(DFT)-based interaction energy components and interaction energies themselves (in kJ/mol) obtained by means of MP2, SCS-MP2, MP2C, and CCSD(T) methods and the aug-cc-pCVXZ (X = D, T, Q, 5) basis sets and the CBS limit (X = 5).

Dimer	$E_{el}^{(1)}$	$E_{ex}^{(1)}$	$E_{ind}^{(2)}$	$E_{ex-ind}^{(2)}$	$E_{disp}^{(2)}$	$E_{ex-disp}^{(2)}$	δE_{HF}	$E_{int}^{SAPT(DFT)}$	E_{int}^{MP2}	$E_{int}^{SCS-MP2}$	E_{int}^{MP2C}	$E_{int}^{CCSD(T)}$
aug-cc-pCVDZ												
DUCBUA	1.852	2.106	-0.772	0.388	-3.607	0.151	-0.090	0.027	-0.546	0.328	0.006	
PH_3	-0.690	3.849	-0.629	0.408	-3.689	0.256	-0.529	-1.023	-1.029	-0.243	-0.394	-1.043
$PMeH_2$	-1.630	5.324	-0.883	0.633	-4.983	0.379	-0.724	-1.884	-1.905	-0.820	-1.061	-1.861
PMe_2H	-2.458	7.073	-1.249	0.957	-6.517	0.529	-0.937	-2.602	-2.741	-1.305	-1.599	-2.587
P_3H_5-T	-1.083	7.437	-1.562	1.060	-6.860	0.469	-1.032	-1.571	-2.405	-0.828	-0.817	-2.063
P_3H_5-C	-1.760	10.950	-2.579	1.773	-9.756	0.665	-1.619	-2.326	-3.937	-1.474	-1.082	-2.807
aug-cc-pCVTZ												
DUCBUA	1.884	2.101	-0.759	0.378	-3.805	0.170	-0.086	-0.116	-0.626	0.276	-0.129	
PH_3	-0.626	3.878	-0.635	0.411	-4.035	0.306	-0.524	-1.225	-1.281	-0.468	-0.705	
$PMeH_2$	-1.575	5.361	-0.900	0.648	-5.408	0.447	-0.717	-2.144	-2.200	-1.089	-1.436	
PMe_2H	-2.408	7.123	-1.293	1.006	-7.028	0.617	-0.928	-2.911	-3.075	-1.615	-2.037	
P_3H_5-T	-1.014	7.479	-1.587	1.084	-7.437	0.552	-1.024	-1.947	-2.835	-1.203	-1.355	
P_3H_5-C	-1.660	11.023	-2.614	1.808	-10.590	0.782	-1.605	-2.857	-4.599	-2.046	-1.865	
aug-cc-pCVQZ												
DUCBUA	1.879	2.103	-0.756	0.378	-3.857	0.178	-0.086	-0.162	-0.649	0.258	-0.170	
PH_3	-0.636	3.880	-0.632	0.410	-4.118	0.322	-0.524	-1.299	-1.353	-0.538	-0.798	
$PMeH_2$	-1.574	5.364	-0.898	0.648	-5.508	0.468	-0.718	-2.218	-2.292	-1.182	-1.557	
PMe_2H	-2.403	7.128	-1.291	1.000	-7.146	0.643	-0.928	-2.991	-3.184	-1.727	-2.185	
P_3H_5-T	-1.028	7.486	-1.584	1.084	-7.571	0.578	-1.024	-2.060	-2.944	-1.306	-1.493	
P_3H_5-C	-1.671	11.038	-2.613	1.809	-10.786	0.818	-1.605	-3.010	-4.774	-2.216	-2.076	
aug-cc-pCV5Z												
DUCBUA	1.875	2.102	-0.755	0.377	-3.872	0.181	-0.086	-0.178	-0.653	0.256	-0.183	
PH_3	-0.638	3.882	-0.632	0.410	-4.143	0.328	-0.524	-1.318	-1.376	-0.561	-0.821	
$PMeH_2$	-1.576	5.367	-0.899	0.648	-5.540	0.476	-0.718	-2.242	-2.326	-1.218	1.587	
PMe_2H	-2.405	7.135	-1.293	1.007	-7.186	0.654	-0.927	-3.017	-3.226	-1.773	-2.219	
P_3H_5-T	-1.031	7.488	-1.585	1.084	-7.615	0.587	-1.024	-2.096	-2.980	-1.344	-1.532	
P_3H_5-C	-1.677	11.044	-2.613	1.810	-10.853	0.832	-1.606	-3.063	-4.842	-2.285	-2.148	
aug-cc-pCV5Z $\longrightarrow$ CBS limit												
DUCBUA	1.875	2.102	-0.755	0.377	-3.888	0.184	-0.086	-0.191	-0.656	0.255	-0.189	
PH_3	-0.638	3.882	-0.632	0.410	-4.169	0.334	-0.524	-1.337	-1.398	-0.584	-0.842	
$PMeH_2$	-1.576	5.367	-0.899	0.648	-5.574	0.484	-0.718	-2.268	-2.359	-1.253	-1.616	
PMe_2H	-2.405	7.135	-1.293	1.007	-7.228	0.665	-0.927	-3.046	-3.269	-1.820	-2.252	
P_3H_5-T	-1.031	7.488	-1.585	1.084	-7.661	0.596	-1.024	-2.133	-3.016	-1.380	-1.571	
P_3H_5-C	-1.677	11.044	-2.613	1.810	-10.923	0.847	-1.606	-3.118	-4.909	-2.353	-2.217	

Table S3: Differences between values of SAPT(DFT)-based interaction energy components and MP2, SCS-MP2, MP2C, and CCSD(T) supermolecular interaction energies (in kJ/mol) obtained by means of no-core and core correlation approaches.

Dimer	$E_{elst}^{(1)}$	$E_{exch}^{(1)}$	$E_{ind}^{(2)}$	$E_{exch-ind}^{(2)}$	$E_{disp}^{(2)}$	$E_{exch-disp}^{(2)}$	δE_{HF}	E_{int}^{SAPT}	E_{int}^{MP2}	$E_{int}^{SCS-MP2}$	E_{int}^{MP2C}	$E_{int}^{CCSD(T)}$
aug-cc-pVDZ vs aug-cc-pCVDZ												
DUCBUA	0.008	0.001	0.002	0.002	0.009	0.001	0.001	0.001	0.019	0.013	0.021	
PH_3	0.011	0.002	0.001	0.000	0.005	0.001	0.002	0.010	0.018	0.014	0.025	0.013
$PMeH_2$	0.007	0.003	0.001	0.001	0.008	0.002	0.003	0.005	0.015	0.010	0.026	0.010
PMe_2H	0.006	0.004	0.003	0.003	0.012	0.003	0.004	0.006	0.012	0.007	0.027	0.009
P_3H_5-T	0.015	0.003	0.002	0.002	0.014	0.002	0.004	0.020	0.046	0.036	0.051	0.025
P_3H_5-C	0.014	0.005	0.003	0.003	0.025	0.004	0.006	0.023	0.067	0.051	0.068	0.029
CBS limit vs CBS limit (core)												
DUCBUA	0.001	0.000	0.000	0.001	0.026	0.001	0.002	0.023	0.009	0.021	0.007	
PH_3	0.001	0.001	0.002	0.002	0.012	0.001	0.002	0.009	0.048	0.038	0.026	
$PMeH_2$	0.000	0.001	0.001	0.003	0.024	0.001	0.002	0.022	0.060	0.048	0.030	
PMe_2H	0.001	0.004	0.001	0.003	0.032	0.006	0.004	0.019	0.075	0.062	0.036	
P_3H_5-T	0.004	0.000	0.003	0.005	0.017	0.001	0.004	0.018	0.117	0.092	0.060	
P_3H_5-C	0.003	0.002	0.004	0.007	0.046	0.005	0.005	0.040	0.201	0.159	0.103	

Table S4: Cartesian coordinates of the fully optimized dimer of PH_2CH_3.

p	-0.205110	-0.202463	-0.418447
p	4.128665	-0.413433	-1.815538
c	1.102377	0.284897	0.807012
h	0.643844	-0.831565	-1.358922
h	-0.247831	1.011340	-1.143154
h	3.101053	-1.180540	-1.218423
c	3.048383	0.874815	-2.604334
h	4.416197	0.285960	-0.620332
h	0.662430	0.976189	1.523985
h	1.415081	-0.605464	1.350125
h	1.974577	0.744973	0.349956
h	3.681143	1.690355	-2.950743
h	2.565333	0.433919	-3.474834
h	2.285333	1.267747	-1.937504

Table S5: Cartesian coordinates of the fully optimized dimer of $PH(CH_3)_2$.

p	-0.207332	-0.517728	-0.416433
p	4.056434	-0.682521	-1.961446
c	1.119184	0.019631	0.758120
h	0.644690	-0.874631	-1.488743
c	-0.712597	1.140230	-1.068081
h	3.082923	-1.276208	-1.123007
c	2.966291	0.629662	-2.680986
c	4.901834	0.321095	-0.654994
h	0.647246	0.495721	1.617554
h	1.667396	-0.851431	1.114821
h	1.817704	0.721187	0.303273
h	3.587106	1.318469	-3.253827
h	2.248795	0.176041	-3.363591
h	2.428907	1.189043	-1.915931
h	-1.269602	1.662516	-0.290618
h	0.140199	1.749857	-1.364259
h	-1.374010	1.009016	-1.923409
h	5.611309	0.991861	-1.138939
h	4.202305	0.910782	-0.063762
h	5.462094	-0.339194	0.005610