Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Existence of Noble Gas Inserted Phosphorus Fluorides: $FNgPF_2$ and $FNgPF_4$ with Ng–P Covalent Bond (Ng = Ar, Kr, Xe and Rn)

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Figure S1. The plots of deformation density ($\Delta\rho(r)$) for $FXePF_2$ and $FXePF_4$ molecules considering FXe as one fragment and PF_2 or PF_4 as another fragment at the B3LYP-D3/TZ2P level of theory; in $FNgPF_2$ molecules, $\Delta\rho_{1\alpha}(r)$ and $\Delta\rho_{1\beta}(r)$ correspond to (FNg ← PF_n) σ-donation and (FNg → PF_n) σ-back donation, respectively; $\Delta\rho_{2\alpha}(r)$, $\Delta\rho_{3\alpha}(r)$, $\Delta\rho_{2\beta}(r)$, and $\Delta\rho_{3\beta}(r)$ refer to the (FNg → PF_n) π-back donations; $\Delta\rho_{4\alpha}(r)$ and $\Delta\rho_{4\beta}(r)$ refers to (FNg → PF_n) σ-back donation. In $FNgPF_4$ systems, $\Delta\rho_{1\alpha}(r)$ and $\Delta\rho_{1\beta}(r)$ correspond to (FNg ← PF_n) σ- donation and (FNg → PF_n) σ-back donation, respectively; $\Delta\rho_{2\alpha}(r)$ represents (FNg → PF_n) σ-back donation; $\Delta\rho_{3\alpha}(r)$, $\Delta\rho_{4\alpha}(r)$, $\Delta\rho_{2\beta}(r)$, and $\Delta\rho_{3\beta}(r)$ correspond to the (FNg → PF_n) π-back donations. The energy of associated orbital terms is provided in kcal mol^{-1}. (An isovalue of 0.001 is used.)

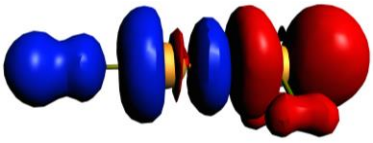
Figure S2. The plots of deformation density ($\Delta\rho(r)$) for $FXePF_2$ and $FXePF_4$ molecules considering FXe^- as one fragment and PF_2^+ or PF_4^+ as another fragment at the B3LYP-D3/TZ2P level of theory, where the deformation density, $\Delta\rho_1(r)$ corresponds to the (FNg^- → PF_n^+) σ-donation; $\Delta\rho_2(r)$ and $\Delta\rho_3(r)$ refer to (FNg^- → PF_n^+) π-donation; $\Delta\rho_4(r)$ represents the (FNg^- ← PF_n^+) σ-back donation; $\Delta\rho_5(r)$ corresponds to (FNg^- ← PF_n^+) π-back donation; all other $\Delta\rho_i(r)$ (i > 5) contributes negligibly. The energy of associated orbital terms is provided in kcal mol^{-1}. (An isovalue of 0.001 is used.)

Figure S3. The plots of deformation density ($\Delta\rho(r)$) for $FXePF_2$ and $FXePF_4$ molecules considering FXe^+ as one fragment and PF_2^- or PF_4^- as another fragment at the B3LYP-D3/TZ2P level of theory, where the deformation density, $\Delta\rho_1(r)$ corresponds to the (FNg^+ ← PF_n^-) σ-donation; $\Delta\rho_2(r)$ and $\Delta\rho_3(r)$ refer to (FNg^+ → PF_n^-) π-back donations; $\Delta\rho_4(r)$ represents the σ-back donation (FNg^+ → PF_n^-); $\Delta\rho_5(r)$ corresponds to (FNg^+ → PF_n^-) π-back donation; all other $\Delta\rho_i(r)$ (i > 5) contributes negligibly. The energy of associated orbital terms is provided in kcal mol^{-1}. (An isovalue of 0.001 is used.)

List of Tables:

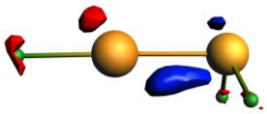
Figure S1. The plots of deformation density ($\Delta\rho(r)$) for $FXePF_2$ and $FXePF_4$ molecules considering FXe as one fragment and PF_2 or PF_4 as another fragment at the B3LYP-D3/TZ2P level of theory; in $FNgPF_2$ molecules, $\Delta\rho_{1\alpha}(r)$ and $\Delta\rho_{1\beta}(r)$ correspond to (FNg ← PF_n) σ-donation and (FNg → PF_n) σ-back donation, respectively; $\Delta\rho_{2\alpha}(r)$, $\Delta\rho_{3\alpha}(r)$, $\Delta\rho_{2\beta}(r)$, and $\Delta\rho_{3\beta}(r)$ refer to the (FNg → PF_n) π-back donations; $\Delta\rho_{4\alpha}(r)$ and $\Delta\rho_{4\beta}(r)$ refers to (FNg → PF_n) σ-back donation. In $FNgPF_4$ systems, $\Delta\rho_{1\alpha}(r)$ and $\Delta\rho_{1\beta}(r)$ correspond to (FNg ← PF_n) σ-donation and (FNg → PF_n) σ-back donation, respectively; $\Delta\rho_{2\alpha}(r)$ represents (FNg → PF_n) σ-back donation; $\Delta\rho_{3\alpha}(r)$, $\Delta\rho_{4\alpha}(r)$, $\Delta\rho_{2\beta}(r)$, and $\Delta\rho_{3\beta}(r)$ correspond to the (FNg → PF_n) π-back donations. The energy of associated orbital terms is provided in kcal mol^{-1}. (An isovalue of 0.001 is used.)

$FXePF_2$ ($FXe + PF_2$)



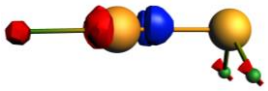
$\Delta\rho_{1\alpha}(r)$

$\Delta E_{1\alpha}^{orb}$ = –41.7



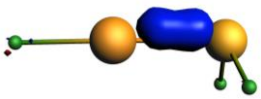
$\Delta\rho_{2\alpha}(r)$

$\Delta E_{2\alpha}^{orb}$ = –1.8



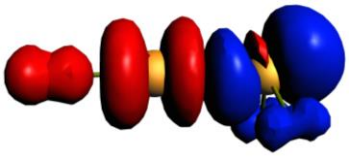
$\Delta\rho_{3\alpha}(r)$

$\Delta E_{3\alpha}^{orb}$ = –1.6



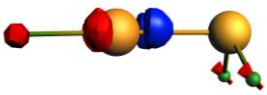
$\Delta\rho_{4\alpha}(r)$

$\Delta E_{4\alpha}^{orb}$ = –1.3



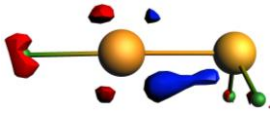
$\Delta\rho_{1\beta}(r)$

$\Delta E_{1\beta}^{orb}$ = –24.0



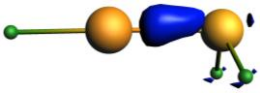
$\Delta\rho_{2\beta}(r)$

$\Delta E_{2\beta}^{orb}$ = –1.4



$\Delta\rho_{3\beta}(r)$

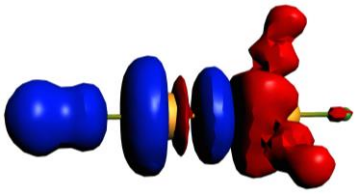
$\Delta E_{3\beta}^{orb}$ = –1.4



$\Delta\rho_{4\beta}(r)$

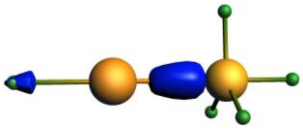
$\Delta E_{4\beta}^{orb}$ = –1.3

$FXePF_4$ ($FXe + PF_4$)



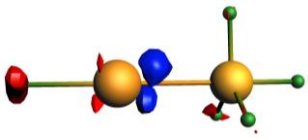
$\Delta\rho_{1\alpha}(\mathbf{r})$

$\Delta E_{1\alpha}^{orb} = -40.1$



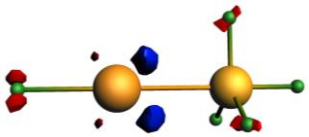
$\Delta\rho_{2\alpha}(\mathbf{r})$

$\Delta E_{2\alpha}^{orb} = -1.6$



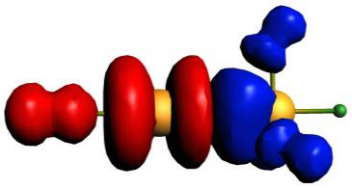
$\Delta\rho_{3\alpha}(\mathbf{r})$

$\Delta E_{3\alpha}^{orb} = -1.2$



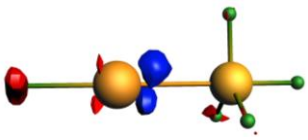
$\Delta\rho_{4\alpha}(\mathbf{r})$

$\Delta E_{4\alpha}^{orb} = -1.2$



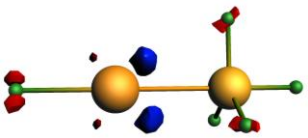
$\Delta\rho_{1\beta}(\mathbf{r})$

$\Delta E_{1\beta}^{orb} = -28.9$



$\Delta\rho_{2\beta}(\mathbf{r})$

$\Delta E_{2\beta}^{orb} = -1.1$

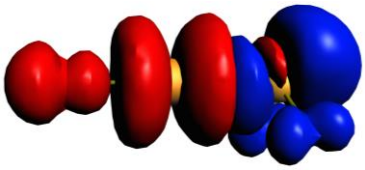


$\Delta\rho_{3\beta}(\mathbf{r})$

$\Delta E_{3\beta}^{orb} = -1.1$

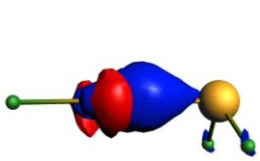
Figure S2. The plots of deformation density ($\Delta\rho(r)$) for $FXePF_2$ and $FXePF_4$ molecules considering FXe^- as one fragment and PF_2^+ or PF_4^+ as another fragment at the B3LYP-D3/TZ2P level of theory, where the deformation density, $\Delta\rho_1(r)$ corresponds to the ($FNg^- \rightarrow PF_n^+$) σ-donation; $\Delta\rho_2(r)$ and $\Delta\rho_3(r)$ refer to ($FNg^- \rightarrow PF_n^+$) π-donation; $\Delta\rho_4(r)$ represents the ($FNg^- \leftarrow PF_n^+$) σ-back donation; $\Delta\rho_5(r)$ corresponds to ($FNg^- \leftarrow PF_n^+$) π-back donation; all other $\Delta\rho_i(r)$ ($i > 5$) contributes negligibly. The energy of associated orbital terms is provided in kcal mol^{-1}. (An isovalue of 0.001 is used.)

$FXePF_2$ (FXe^- + PF_2^+)



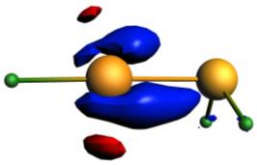
$\Delta\rho_1(r)$

ΔE_1^{orb} = –129.3



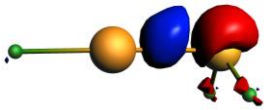
$\Delta\rho_2(r)$

ΔE_2^{orb} = –5.4



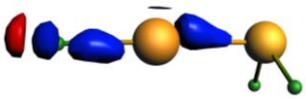
$\Delta\rho_3(r)$

ΔE_3^{orb} = –5.1



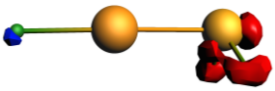
$\Delta\rho_4(r)$

ΔE_4^{orb} = –2.2



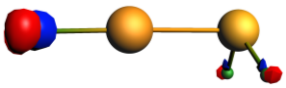
$\Delta\rho_5(r)$

ΔE_5^{orb} = –1.3



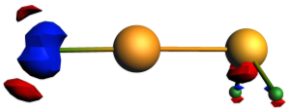
$\Delta\rho_6(r)$

ΔE_6^{orb} = –0.5



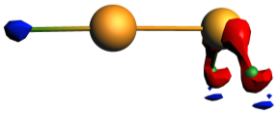
$\Delta\rho_7(r)$

ΔE_7^{orb} = –0.2



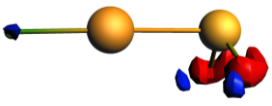
$\Delta\rho_8(r)$

ΔE_8^{orb} = –0.2



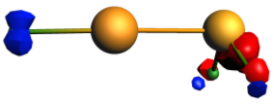
$\Delta\rho_9(r)$

ΔE_9^{orb} = –0.3



$\Delta\rho_{10}(r)$

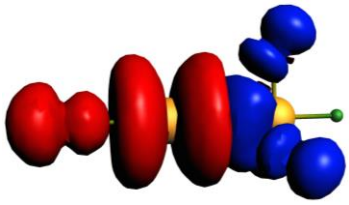
ΔE_{10}^{orb} = –0.1



$\Delta\rho_{11}(r)$

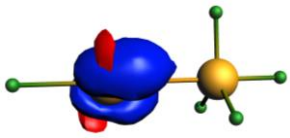
ΔE_{11}^{orb} = –0.2

$FXePF_4$ ($FXe^- + PF_4^+$)



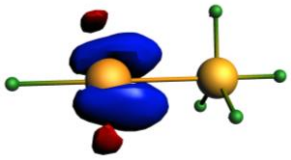
$\Delta\rho_1(\mathbf{r})$

$\Delta E_1^{orb} = -137.5$



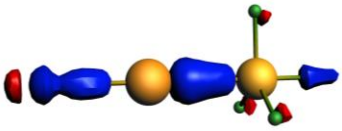
$\Delta\rho_2(\mathbf{r})$

$\Delta E_2^{orb} = -4.2$



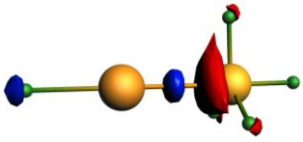
$\Delta\rho_3(\mathbf{r})$

$\Delta E_3^{orb} = -4.2$



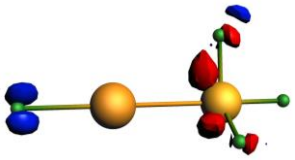
$\Delta\rho_4(\mathbf{r})$

$\Delta E_4^{orb} = -2.4$



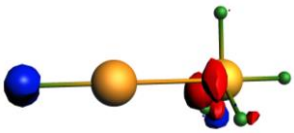
$\Delta\rho_5(\mathbf{r})$

$\Delta E_5^{orb} = -1.4$



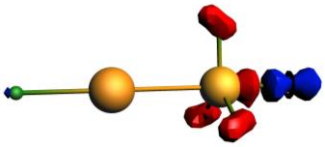
$\Delta\rho_6(\mathbf{r})$

$\Delta E_6^{orb} = -0.3$



$\Delta\rho_7(\mathbf{r})$

$\Delta E_7^{orb} = -0.3$



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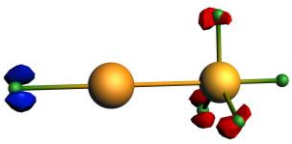
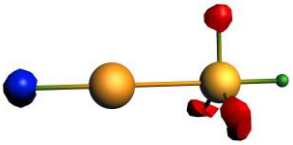
$\Delta E_8^{orb} = -0.4$



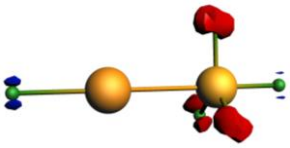
$\Delta\rho_9(\mathbf{r})$

$\Delta E_9^{orb} = -0.5$



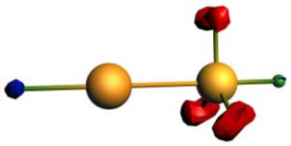
$\Delta\rho_{10}(\mathbf{r})$

$\Delta E_{10}^{orb} = -0.5$



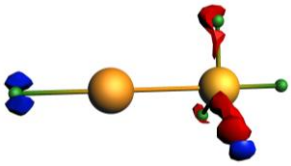
$\Delta\rho_{11}(\mathbf{r})$

$\Delta E_{11}^{orb} = -0.3$



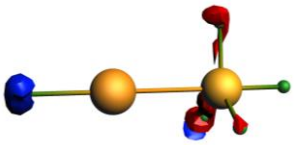
$\Delta\rho_{12}(\mathbf{r})$

$\Delta E_{12}^{orb} = -0.3$



$\Delta\rho_{13}(\mathbf{r})$

$\Delta E_{13}^{orb} = -0.1$

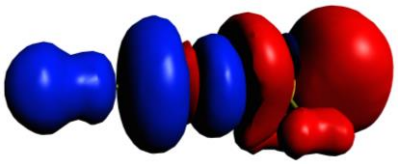


$\Delta\rho_{14}(\mathbf{r})$

$\Delta E_{14}^{orb} = -0.1$

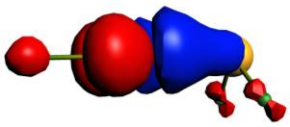
Figure S3. The plots of deformation density ($\Delta\rho(r)$) for $FXePF_2$ and $FXePF_4$ molecules considering FXe^+ as one fragment and PF_2^- or PF_4^- as another fragment at the B3LYP-D3/TZ2P level of theory, where the deformation density, $\Delta\rho_1(r)$ corresponds to the ($FNg^+ \leftarrow PF_n^-$) σ-donation; $\Delta\rho_2(r)$ and $\Delta\rho_3(r)$ refer to ($FNg^+ \rightarrow PF_n^-$) π-back donations; $\Delta\rho_4(r)$ represents the σ-back donation ($FNg^+ \rightarrow PF_n^-$); $\Delta\rho_5(r)$ corresponds to ($FNg^+ \rightarrow PF_n^-$) π-back donation; all other $\Delta\rho_i(r)$ ($i > 5$) contributes negligibly. The energy of associated orbital terms is provided in kcal mol^{-1}. (An isovalue of 0.001 is used.)

$FXePF_2$ ($FXe^+ + PF_2^-$)



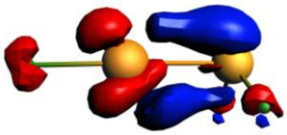
$\Delta\rho_1(r)$

ΔE_1^{orb} = –204.0



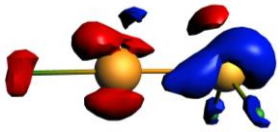
$\Delta\rho_2(r)$

ΔE_2^{orb} = –1.0



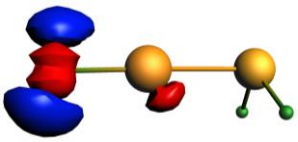
$\Delta\rho_3(r)$

ΔE_3^{orb} = –3.2



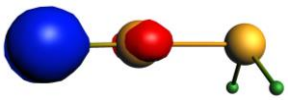
$\Delta\rho_4(r)$

ΔE_4^{orb} = –1.1



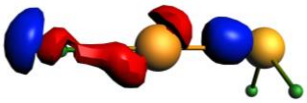
$\Delta\rho_5(r)$

ΔE_5^{orb} = –0.9



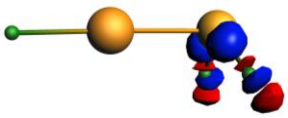
$\Delta\rho_6(r)$

ΔE_6^{orb} = –0.7



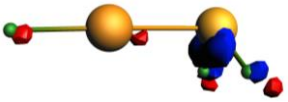
$\Delta\rho_7(r)$

ΔE_7^{orb} = –1.7



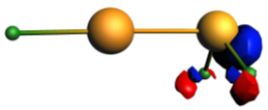
$\Delta\rho_8(r)$

ΔE_8^{orb} = –0.6



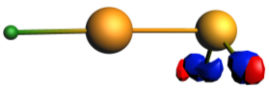
$\Delta\rho_9(r)$

ΔE_9^{orb} = –0.5



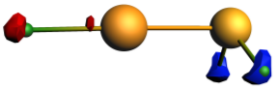
$\Delta\rho_{10}(r)$

ΔE_{10}^{orb} = –0.1



$\Delta\rho_{11}(r)$

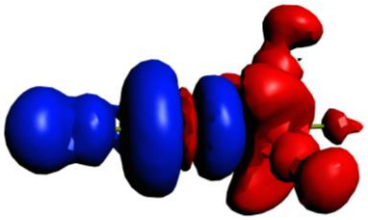
ΔE_{11}^{orb} = –0.3



$\Delta\rho_{12}(r)$

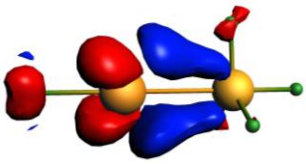
ΔE_{12}^{orb} = –0.3

$FXePF_4$ ($FXe^+ + PF_4^-$)



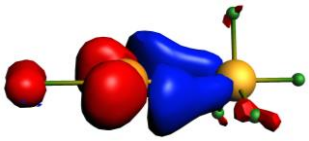
$\Delta\rho_1(r)$

$\Delta E_1^{orb} = -197.7$



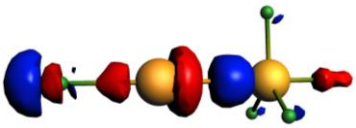
$\Delta\rho_2(r)$

$\Delta E_2^{orb} = -1.2$



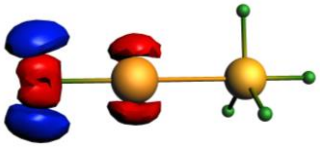
$\Delta\rho_3(r)$

$\Delta E_3^{orb} = -1.2$



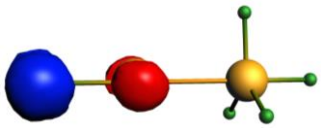
$\Delta\rho_4(r)$

$\Delta E_4^{orb} = -2.6$



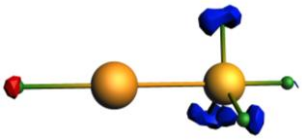
$\Delta\rho_5(r)$

$\Delta E_5^{orb} = -0.7$



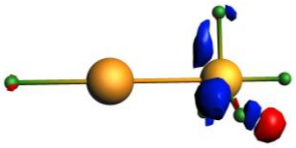
$\Delta\rho_6(r)$

$\Delta E_6^{orb} = -0.7$



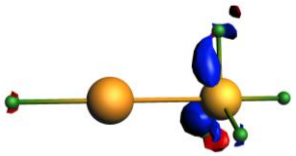
$\Delta\rho_7(r)$

$\Delta E_7^{orb} = -0.7$



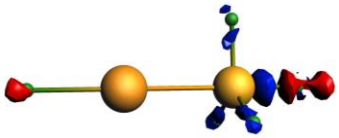
$\Delta\rho_8(r)$

$\Delta E_8^{orb} = -1.0$



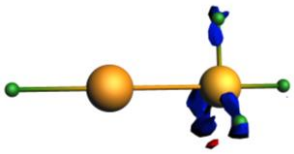
$\Delta\rho_9(r)$

$\Delta E_9^{orb} = -1.0$



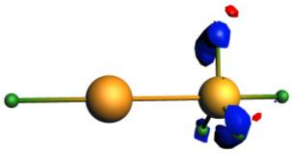
$\Delta\rho_{10}(r)$

$\Delta E_{10}^{orb} = -0.6$



$\Delta\rho_{11}(r)$

$\Delta E_{11}^{orb} = -0.5$



$\Delta\rho_{12}(r)$

$\Delta E_{12}^{orb} = -0.5$

Table S1. Calculated F–Ng, Ng–P Bond Length (R in Å) and F–Ng–P Bond Angles (θ in Degree) Values in $FNgPF_2$ and $FNgPF_4$ (Ng = Ar, Kr, Xe, and Rn) Molecules using B3LYP and MP2 Methods with the DEF2 Basis Set and CCSD(T) Method with AVTZ Basis Set.

Molecule	Parameters	Method	Ar		Kr		Xe		Rn	
			Min	TS	Min	TS	Min	TS	Min	TS
$FNgPF_2$	R(F–Ng)	MP2	2.051	2.291	2.095	2.368	2.164	2.423	2.227	2.471
		B3LYP	2.135	2.474	2.159	2.516	2.198	2.470	2.252	2.499
		CCSD(T)	2.178	...[a]	2.112	...[a]	2.162	...[a]	2.226	...[a]
	R(Ng–P)	MP2	2.266	2.247	2.413	2.379	2.592	2.545	2.690	2.630
		B3LYP	2.435	2.356	2.527	2.461	2.675	2.655	2.765	2.720
		CCSD(T)	2.203	...[a]	2.479	...[a]	2.626	...[a]	2.725	...[a]
	θ(F–Ng–P)	MP2	177.5	118.6	178.1	110.5	178.7	103.5	178.8	99.4
		B3LYP	177.0	104.1	178.3	98.5	179.0	98.9	178.8	95.3
		CCSD(T)	178.9	...[a]	177.2	...[a]	178.4	...[a]	178.5	...[a]
$FNgPF_4$[b]	R(F–Ng)	MP2	2.074	2.344	2.086	2.422	2.145	2.477	2.206	2.515
		B3LYP	2.122	2.450	2.137	2.531	2.169	2.531	2.222	2.553
	R(Ng–P)	MP2	2.255	2.436	2.402	2.557	2.588	2.675	2.688	2.740
		B3LYP	2.403	2.697	2.500	2.807	2.657	2.800	2.749	2.845
	θ(F–Ng–P)	MP2	180.0	134.0	180.0	120.2	180.0	108.1	180.0	102.6
		B3LYP	180.0	114.5	180.0	105.2	180.0	100.0	180.0	96.1

[a]It has not been possible to optimize the transition state of $FNgPF_2$ molecules by using CCSD(T)/AVTZ level of theory.

[b]It has not been possible to optimize the minima and the transition state geometry of $FNgPF_4$ molecules by employing CCSD(T) method with AVTZ basis set.

Table S2. Calculated Values of the Mullikan Charges of Constituent Atoms in $FNgPF_2$ and $FNgPF_4$ (Ng = Ar, Kr, Xe and Rn) Molecules Using the B3LYP and MP2 Methods with DEF2 Basis Set.

$FNgPF_2$	Methods	Ar		Kr		Xe		Rn	
		Min	TS	Min	TS	Min	TS	Min	TS
F^a	MP2	−0.733	−0.880	−0.698	−0.872	−0.654	−0.825	−0.664	−0.826
	B3LYP	−0.651	−0.623	−0.666	−0.681	−0.634	−0.744	−0.640	−0.754
Ng	MP2	0.390	0.308	0.590	0.406	0.624	0.499	0.679	0.549
	B3LYP	0.299	0.123	0.464	0.225	0.548	0.411	0.611	0.469
P	MP2	0.728	0.858	0.529	0.771	0.477	0.648	0.433	0.612
	B3LYP	0.698	0.738	0.582	0.699	0.505	0.616	0.450	0.577
F^b	MP2	−0.193	−0.159	−0.210	−0.169	−0.224	−0.176	−0.224	−0.178
	B3LYP	−0.173	−0.136	−0.191	−0.146	−0.209	−0.163	−0.211	−0.169
$FNgPF_4$	Methods	Ar		Kr		Xe		Rn	
		Min	TS	Min	TS	Min	TS	Min	TS
F^a	MP2	−0.782	−0.912	−0.699	−0.898	−0.638	−0.855	−0.652	−0.853
	B3LYP	−0.684	−0.738	−0.669	−0.760	−0.618	−0.776	−0.625	−0.784
Ng	MP2	0.266	0.147	0.406	0.211	0.484	0.333	0.594	0.411
	B3LYP	0.248	0.098	0.343	0.119	0.445	0.261	0.555	0.339
P	MP2	1.376	1.332	1.220	1.278	1.134	1.142	1.017	1.102
	B3LYP	1.276	1.140	1.240	1.160	1.162	1.116	1.043	1.098
F^b	MP2	−0.184	−0.119	−0.203	−0.122	−0.218	−0.127	−0.210	−0.137
	B3LYP	−0.184	−0.102	−0.202	−0.109	−0.223	−0.128	−0.217	−0.133

[a]It corresponds to the fluorine (F) atom that is bonded to the noble gas (Ng) atom.

[b]It represents the fluorine (F) atom that is bonded to the phosphorous (P) atom.

Table S3. EDA-NOCV Results of $FNgPF_2$ and $FNgPF_4$ (Ng = Ar, Kr, Xe, and Rn) Molecules Considering F^- as One Fragment and $NgPF_2^+$ or $NgPF_4^+$ as Another Fragment at the B3LYP-D3/TZ2P Level of Theory. All Energy Terms are Expressed in kcal mol^{-1}.

Molecule	ΔE^{Pauli} *a*	ΔE^{elstat} *a*	ΔE_T^{orb} *a*	ΔE_1^{orb} *b*	ΔE_2^{orb} *b*	ΔE_3^{orb} *b*	ΔE_4^{orb} *b*	ΔE_5^{orb} *b*	ΔE_{res}^{orb} *b*	ΔE^{disp} *a*	ΔE^{int}
$FArPF_2$	76.2	−145.6 (70.0)	−62.3 (29.9)	−53.5 (85.9)	−2.5 (4.0)	−2.4 (3.9)	−1.7 (3.0)	−0.5 (0.8)	−1.7 (2.7)	−0.2 (0.1)	−131.9
$FKrPF_2$	94.1	−161.8 (69.3)	−71.5 (30.6)	−58.9 (82.4)	−3.7 (5.2)	−3.6 (5.0)	−2.6 (3.6)	−0.5 (0.7)	−2.2 (3.1)	−0.1 (0.0)	−139.3
$FXePF_2$	116.4	−183.0 (69.2)	−81.5 (30.8)	−64.7 (79.4)	−5.1 (6.3)	−5.0 (6.1)	−3.9 (4.8)	−0.7 (0.9)	−2.1 (2.6)	−0.1 (0.0)	−148.2
$FRnPF_2$	110.0	−184.4 (70.7)	−76.3 (29.3)	−60.0 (78.6)	−4.8 (6.3)	−4.7 (6.2)	−3.9 (5.1)	−0.6 (0.8)	−2.3 (3.0)	−0.1 (0.0)	−150.8
$FArPF_4$	68.9	−145.0 (72.2)	−55.5 (27.7)	−46.6 (84.0)	−2.3 (4.1)	−2.3 (4.1)	−1.6 (2.9)	...[c]	−2.7 (4.9)	−0.2 (0.1)	−131.8
$FKrPF_4$	94.2	−167.8 (70.2)	−71.0 (29.7)	−57.9 (81.5)	−3.6 (5.1)	−3.6 (5.1)	−2.6 (3.7)	...[c]	−3.3 (4.6)	−0.1 (0.0)	−144.8
$FXePF_4$	119.3	−193.1 (69.6)	−84.1 (30.3)	−66.6 (79.2)	−5.1 (6.1)	−5.1 (6.1)	−3.9 (4.6)	−0.9 (1.1)	−2.5 (3.0)	−0.1 (0.0)	−158.0
$FRnPF_4$	112.6	−195.5 (71.2)	−78.9 (28.7)	−61.8 (78.3)	−4.9 (6.2)	−4.9 (6.2)	−3.9 (4.9)	−0.9 (1.1)	−2.5 (3.2)	−0.1 (0.0)	−162.0

[a]The values within the parentheses are in percentage and show the contribution towards the total attractive interaction $\Delta E^{elstat} + \Delta E_T^{orb} + \Delta E^{disp}$.

[b]The values within parentheses are the percentage contribution towards the total orbital interaction ΔE_T^{orb}.

[c]The corresponding value is below the cut-off value of ADF to be listed in the EDA-NOCV results.

Table S4. EDA-NOCV Results of $FNgPF_2$ and $FNgPF_4$ (Ng = Ar, Kr, Xe, and Rn) Molecules Considering FNg as One Fragment and PF_2 or PF_4 as Another Fragment at the B3LYP-D3/TZ2P Level of Theory. All Energy Terms are Expressed in kcal mol^{-1}.

Molecule	ΔE^{Pauli} [a]	ΔE^{elstat} [a]	ΔE_T^{orb} [a]	ΔE_1^{orb}		ΔE_2^{orb}		ΔE_3^{orb}		ΔE_4^{orb}		ΔE_{res}^{orb} [b]	ΔE^{disp} [a]	ΔE^{int}
				ΔE_α^{orb} [b]	ΔE_β^{orb} [b]	ΔE_α^{orb} [b]	ΔE_β^{orb} [b]	ΔE_α^{orb} [b]	ΔE_β^{orb} [b]	ΔE_α^{orb} [b]	ΔE_β^{orb} [b]			
$FArPF_2$	134.5	–63.4 (44.8)	–77.2 (54.6)	–56.4 (73.1)	–8.7 (11.3)	–2.5 (3.2)	–1.5 (1.9)	–1.5 (1.9)	–1.3 (1.7)	–1.7 (2.2)	–1.6 (2.1)	–2.0 (2.6)	–0.9 (0.6)	–7.0
$FKrPF_2$	127.4	–66.2 (46.2)	–76.4 (53.3)	–49.5 (64.8)	–15.4 (20.2)	–2.0 (2.6)	–1.4 (1.8)	–1.6 (2.1)	–1.5 (2.0)	–1.5 (2.0)	–1.4 (1.8)	–2.1 (2.7)	–0.8 (0.6)	–16.0
$FXePF_2$	123.7	–68.9 (47.2)	–76.2 (52.2)	–41.7 (54.7)	–24.0 (31.5)	–1.8 (2.4)	–1.4 (1.8)	–1.6 (2.1)	–1.4 (1.8)	–1.3 (1.7)	–1.3 (1.7)	–1.7 (2.2)	–0.9 (0.6)	–22.2
$FRnPF_2$	113.8	–67.1 (48.9)	–69.2 (50.4)	–34.4 (49.7)	–25.7 (37.1)	–1.4 (2.0)	–1.3 (1.9)	–1.5 (2.2)	–1.3 (1.9)	...[c]	–1.1 (1.6)	–2.5 (3.6)	–1.0 (0.7)	–23.5
$FArPF_4$	148.2	–71.5 (44.0)	–89.8 (55.3)	–67.4 (75.1)	–10.8 (12.0)	–2.9 (3.2)	–1.1 (1.2)	–1.3 (1.4)	–1.1 (1.2)	–1.3 (1.4)	–0.8 (0.9)	–3.1 (3.5)	–1.2 (0.7)	–14.3
$FKrPF_4$	132.5	–70.0 (45.6)	–82.4 (53.7)	–52.8 (64.1)	–18.8 (22.8)	–2.1 (2.5)	–1.2 (1.5)	–1.4 (1.7)	–1.2 (1.5)	–1.4 (1.7)	...[c]	–3.5 (4.2)	–1.0 (0.7)	–21.0
$FXePF_4$	120.7	–68.2 (46.3)	–78.0 (52.9)	–40.1 (51.4)	–28.9 (37.1)	–1.6 (2.1)	–1.1 (1.4)	–1.2 (1.5)	–1.1 (1.4)	–1.2 (1.5)	...[c]	–2.8 (3.6)	–1.2 (0.8)	–26.7
$FRnPF_4$	108.8	–65.2 (47.6)	–70.4 (51.4)	–31.6 (44.9)	–31.3 (44.5)	–1.3 (1.8)	–1.0 (1.4)	–1.0 (1.4)	–1.0 (1.4)	–1.0 (1.4)	...[c]	–2.2 (3.1)	–1.4 (1.0)	–28.1

[a]The values within the parentheses are in percentage and show the contribution towards the total attractive interaction $\Delta E^{elstat} + \Delta E_T^{orb} + \Delta E^{disp}$.

[b]The values within parentheses are the percentage contribution towards the total orbital interaction ΔE_T^{orb};

[c]The corresponding value is below the cut-off value of ADF to be listed in the EDA-NOCV results.

Table S5. EDA-NOCV Results of $FNgPF_2$ and $FNgPF_4$ (Ng = Ar, Kr, Xe, and Rn) Molecules Considering FNg^- as One Fragment and PF_2^+ or PF_4^+ as Another Fragment at the B3LYP-D3/TZ2P Level of Theory. All Energy Terms are Expressed in kcal mol^{-1}.

Molecule	ΔE^{Pauli} [a]	ΔE^{elstat} [a]	ΔE_T^{orb} [a]	ΔE_i^{orb} [b]												ΔE^{disp} [a]	ΔE^{int}
				ΔE_1	ΔE_2	ΔE_3	ΔE_4	ΔE_5	ΔE_6	ΔE_7	ΔE_8	ΔE_9	ΔE_{10}	ΔE_{11}	ΔE_{12}	ΔE_{res}	
$FArPF_2$	97.3	−136.9 (53.8)	−116.6 (45.8)	−99.0 (84.9)	−5.3 (4.5)	−4.9 (4.2)	−2.5 (2.1)	−2.8 (2.4)	−0.2 (0.2)	−0.3 (0.3)	−0.6 (0.5)	...[c]	...[c]	...[c]	...[c]	−1.0 (0.9)	−0.9 (0.4)	−157.2
$FKrPF_2$	107.8	−149.2 (53.8)	−127.4 (45.9)	−110.8 (87.0)	−5.1 (4.0)	−5.0 (3.9)	−1.0 (0.8)	−3.1 (2.4)	−0.2 (0.2)	−0.2 (0.2)	−0.6 (0.5)	−0.2 (0.2)	...[c]	...[c]	...[c]	−1.2 (0.9)	−0.8 (0.3)	−169.6
$FXePF_2$	128.1	−162.6 (52.7)	−145.3 (47.1)	−129.3 (89.0)	−5.4 (3.7)	−5.1 (3.5)	−2.2 (1.5)	−1.3 (0.9)	−0.5 (0.3)	−0.2 (0.1)	−0.2 (0.1)	−0.3 (0.2)	−0.1 (0.1)	−0.2 (0.1)	...[c]	−0.5 (0.3)	−0.9 (0.3)	−180.6
$FRnPF_2$	132.3	−165.5 (52.5)	−148.7 (47.2)	−134.3 (90.3)	−5.1 (3.4)	−4.7 (3.2)	−1.8 (1.2)	−1.1 (0.7)	−0.4 (0.3)	−0.2 (0.1)	−0.2 (0.1)	−0.2 (0.1)	−0.1 (0.1)	−0.1 (0.1)	...[c]	−0.5 (0.3)	−1.0 (0.3)	−182.9
$FArPF_4$	94.8	−142.2 (55.9)	−110.9 (43.6)	−93.2 (84.0)	−3.7 (3.3)	−4.4 (4.0)	−4.4 (4.0)	−2.0 (1.8)	−0.3 (0.3)	−0.3 (0.3)	−0.5 (0.5)	−0.4 (0.4)	...[c]	...[c]	...[c]	−1.7 (1.5)	−1.2 (0.5)	−159.5
$FKrPF_4$	105.8	−159.7 (54.8)	−130.4 (44.8)	−113.2 (86.8)	−4.2 (3.2)	−4.2 (3.2)	−3.0 (2.3)	−1.7 (1.3)	−0.2 (0.2)	−0.2 (0.2)	−0.4 (0.3)	−0.5 (0.4)	−0.5 (0.4)	...[c]	...[c]	−2.3 (1.8)	−1.1 (0.4)	−185.3
$FXePF_4$	124.7	−176.3 (53.3)	−153.5 (46.4)	−137.5 (89.6)	−4.2 (2.7)	−4.2 (2.7)	−2.4 (1.6)	−1.4 (0.9)	−0.3 (0.2)	−0.3 (0.2)	−0.4 (0.3)	−0.5 (0.3)	−0.5 (0.3)	−0.3 (0.2)	−0.3 (0.2)	−1.2 (0.8)	−1.2 (0.4)	−206.2
$FRnPF_4$	129.4	−181.1 (53.1)	−158.8 (46.5)	−144.6 (91.1)	−3.8 (2.4)	−3.8 (2.4)	−2.3 (1.4)	−1.0 (0.6)	−0.3 (0.2)	−0.3 (0.2)	−0.4 (0.3)	−0.4 (0.3)	−0.4 (0.3)	−0.3 (0.2)	−0.3 (0.2)	−0.9 (0.6)	−1.4 (0.4)	−211.8

[a]The values within the parentheses are in percentage and show the contribution towards the total attractive interaction $\Delta E^{elstat} + \Delta E_T^{orb} + \Delta E^{disp}$.

[b]The values within parentheses are the percentage contribution towards the total orbital interaction ΔE_T^{orb}.

[c]The corresponding value is below the cut-off value of ADF to be listed in the EDA-NOCV results.

Table S6. EDA-NOCV Results of $FNgPF_2$ and $FNgPF_4$ (Ng = Ar, Kr, Xe, and Rn) Molecules Considering FNg^+ as One Fragment and PF_2^- or PF_4^- as Another Fragment at the B3LYP-D3/TZ2P Level of Theory. All Energy Terms are Expressed in kcal mol^{-1}.

Molecule	ΔE^{Pauli} [a]	ΔE^{elstat} [a]	ΔE_T^{orb} [a]	ΔE_i^{orb} [b]												ΔE^{disp} [a]	ΔE^{int}
				ΔE_1	ΔE_2	ΔE_3	ΔE_4	ΔE_5	ΔE_6	ΔE_7	ΔE_8	ΔE_9	ΔE_{10}	ΔE_{11}	ΔE_{12}	ΔE_{res}	
$FArPF_2$	231.1	–254.0 (45.1)	–308.7 (54.8)	–297.3 (96.3)	–2.9 (0.9)	–0.2 (0.1)	–1.0 (0.3)	–2.0 (0.6)	–1.3 (0.4)	–1.4 (0.5)	–0.3 (0.1)	–0.4 (0.1)	–0.3 (0.1)	–0.3 (0.1)	–0.3 (0.1)	–1.0 (0.3)	–0.9 (0.2)	–332.5
$FKrPF_2$	226.4	–268.1 (50.4)	–262.8 (49.4)	–251.3 (95.6)	–2.9 (1.1)	–0.7 (0.3)	–1.1 (0.4)	–1.2 (0.5)	–0.9 (0.3)	–1.6 (0.6)	–0.5 (0.2)	–0.5 (0.2)	–0.2 (0.1)	–0.3 (0.1)	–0.3 (0.1)	–1.3 (0.5)	–0.8 (0.2)	–305.4
$FXePF_2$	223.9	–278.5 (56.3)	–215.7 (43.6)	–204.0 (94.6)	–1.0 (0.5)	–3.2 (1.5)	–1.1 (0.5)	–0.9 (0.4)	–0.7 (0.3)	–1.7 (0.8)	–0.6 (0.3)	–0.5 (0.2)	–0.1 (0.0)	–0.3 (0.1)	–0.3 (0.1)	–1.3 (0.6)	–0.9 (0.2)	–271.2
$FRnPF_2$	208.4	–280.4 (60.0)	–185.9 (39.8)	–174.6 (93.9)	–1.1 (0.6)	–3.2 (1.7)	–1.1 (0.6)	–0.8 (0.4)	–0.7 (0.4)	–1.5 (0.8)	–0.6 (0.3)	–0.5 (0.3)	–0.2 (0.1)	...[c]	...[c]	–1.6 (0.9)	–1.0 (0.2)	–259.0
$FArPF_4$	226.0	–236.9 (41.6)	–331.1 (58.2)	–316.7 (95.7)	–0.2 (0.1)	–0.2 (0.1)	–3.5 (1.1)	–1.7 (0.5)	–1.7 (0.5)	–0.6 (0.2)	–0.4 (0.1)	–0.8 (0.2)	–0.8 (0.2)	–0.7 (0.2)	–0.6 (0.2)	–3.2 (1.0)	–1.2 (0.2)	–343.2
$FKrPF_4$	218.3	–250.9 (48.1)	–269.3 (51.7)	–254.6 (94.5)	–0.9 (0.3)	–0.9 (0.3)	–3.0 (1.1)	–1.0 (0.4)	–1.0 (0.4)	–0.6 (0.2)	–0.9 (0.3)	–0.9 (0.3)	–0.7 (0.3)	–0.6 (0.2)	–0.6 (0.2)	–3.6 (1.3)	–1.1 (0.2)	–302.9
$FXePF_4$	207.8	–255.7 (54.6)	–211.5 (45.2)	–197.7 (93.5)	–1.2 (0.6)	–1.2 (0.6)	–2.6 (1.2)	–0.7 (0.3)	–0.7 (0.3)	–0.7 (0.3)	–1.0 (0.5)	–1.0 (0.5)	–0.6 (0.3)	–0.5 (0.2)	–0.5 (0.2)	–3.1 (1.5)	–1.2 (0.3)	–260.6
$FRnPF_4$	188.6	–255.0 (58.6)	–178.5 (41.0)	–165.6 (92.8)	–1.1 (0.6)	–1.1 (0.6)	–2.3 (1.3)	–0.7 (0.4)	–0.7 (0.4)	–1.0 (0.6)	–1.0 (0.6)	–0.7 (0.4)	–0.6 (0.3)	–0.5 (0.3)	–0.5 (0.3)	–2.7 (1.5)	–1.4 (0.3)	–246.3

[a]The values within the parentheses are in percentage and show the contribution towards the total attractive interaction $\Delta E^{elstat} + \Delta E_T^{orb} + \Delta E^{disp}$.

[b]The values within parentheses are the percentage contribution towards the total orbital interaction ΔE_T^{orb}.

[c]The corresponding value is below the cut-off value of ADF to be listed in the EDA-NOCV results.