Electronic Supplementary Information

Elusive Hypervalent Phosphorus…π Interactions: Evidence for Paradigm Transformation from Hydrogen to Phosphorus Bonding at Low Temperatures

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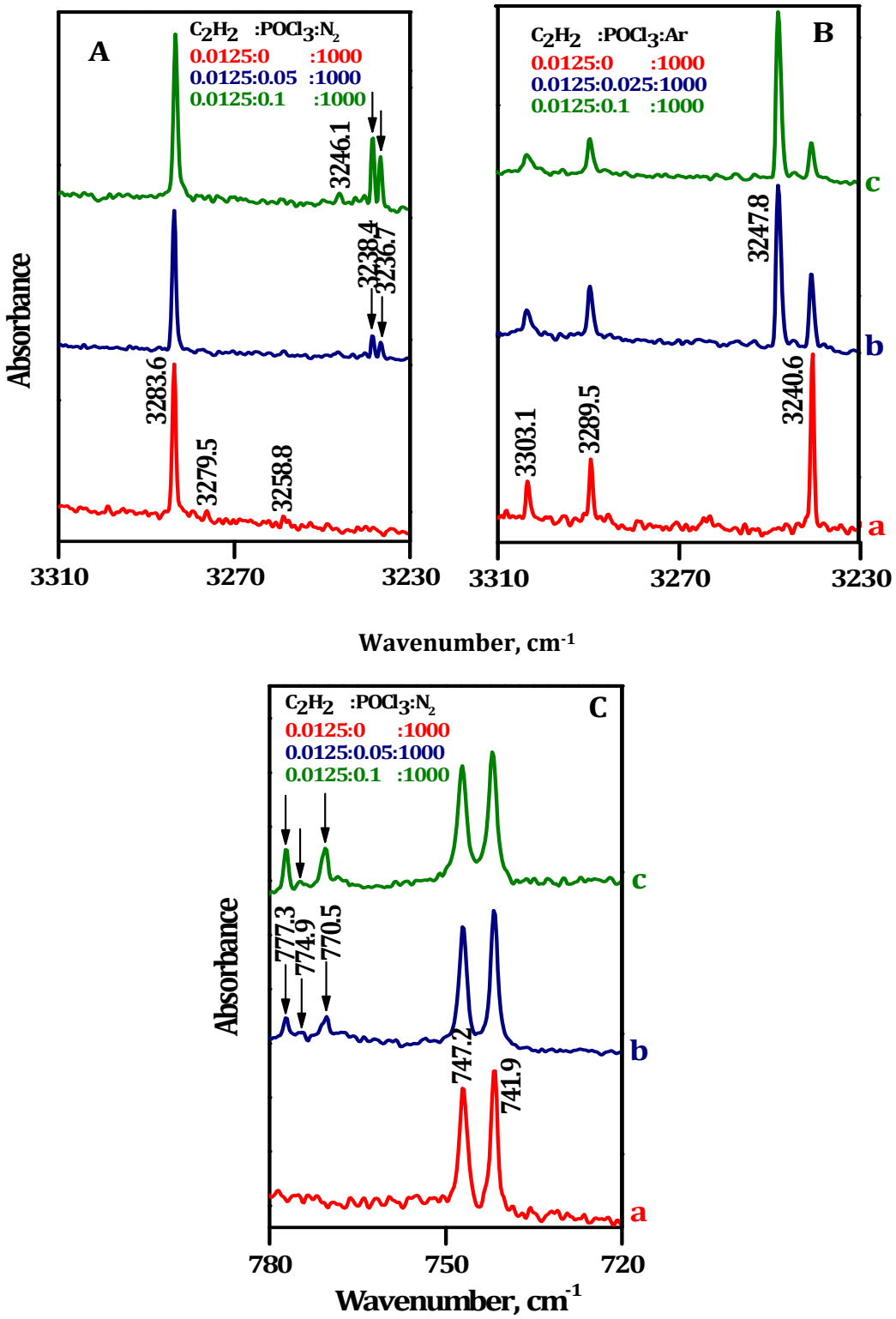

Figure S1. Infrared spectra of C-H stretching and bending region of C_2H_2. Grid A, Cand Grid B corresponds to $POCl_3$ with C_2H_2in N_2 and Ar matrixes, respectively. Spectra are recorded at 12 K after annealing the matrix at 30 K(N_2) and 35 K (Ar).

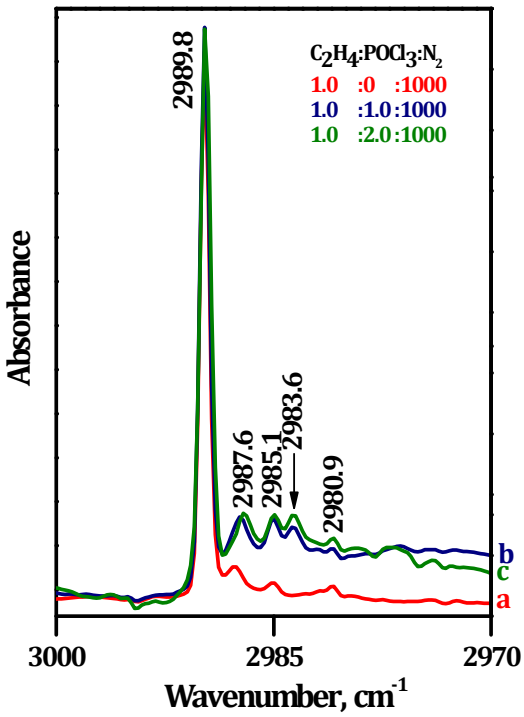

Figure S2. Infrared spectra of C-H stretching region of C_2H_4 in N_2 matrix, spanning the region 3000-2970 cm^{-1}. All spectra are recorded at 12 K after annealing the matrix at 30 K.

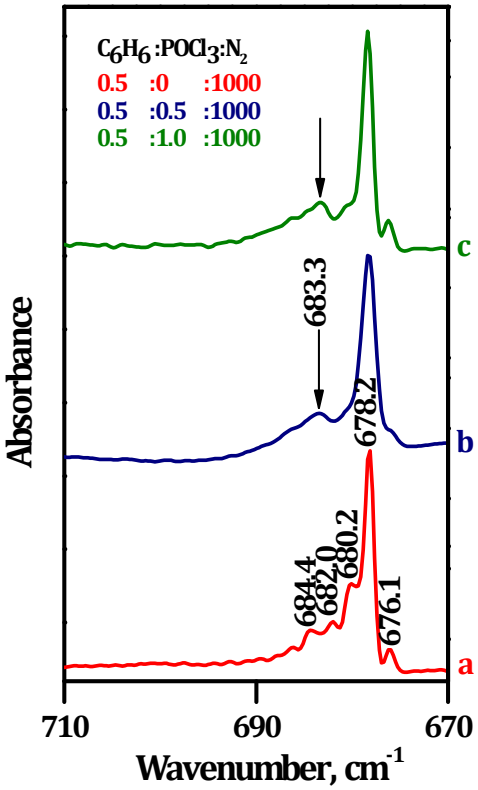

Figure S3. Infrared spectra of C-H bending region of C_6H_6 in N_2 matrix, spanning the region 710-670 cm^{-1}. All spectra are recorded at 12 K after annealing at 30 K.

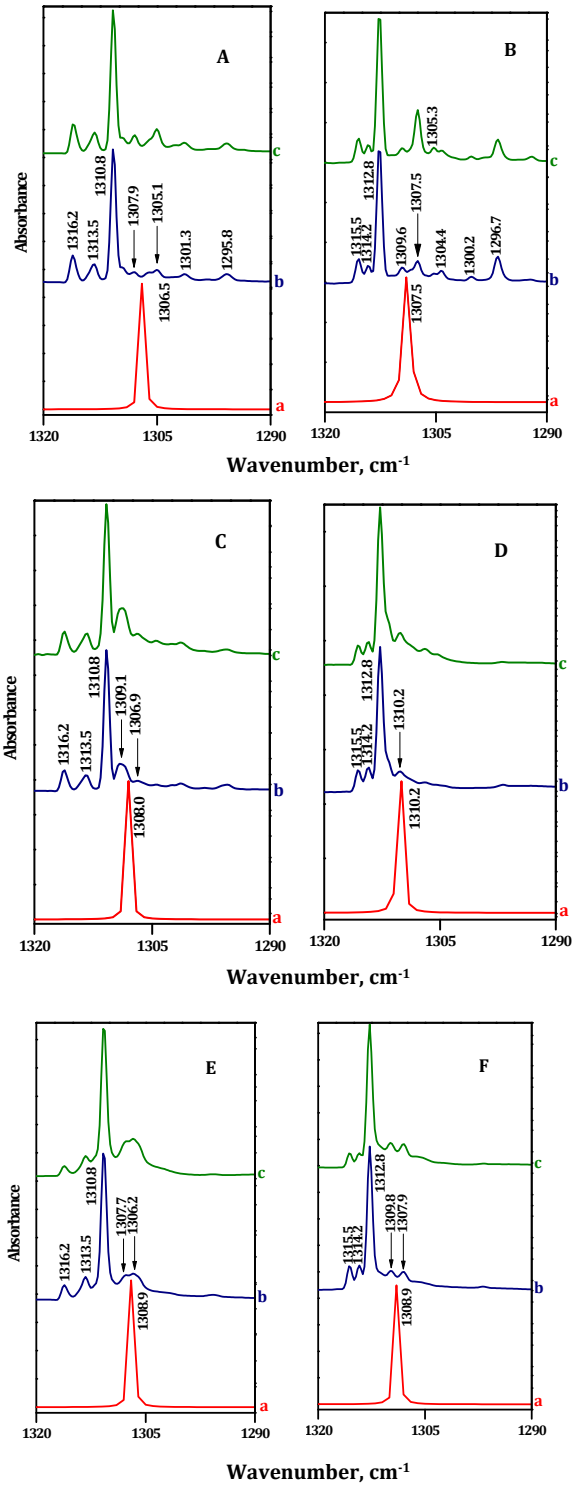

Figure S4. Infrared spectra in the P=O stretching region of $POCl_3$. Grid A, C, E and Grid B, D, F corresponds to the co-deposition experiments of $POCl_3$ with C_2H_2,C_2H_4,C_6H_6 in N_2 and Ar matrixes respectively. All spectra were recorded at 12 K after annealing at 30 K (N_2) and 35 K (Ar). Trace 'a' in all the grids correspond to computed scaled spectra and trace 'b' and 'c' correspond to variation of concentration of the π-donors for the fixed concentration of $POCl_3$.

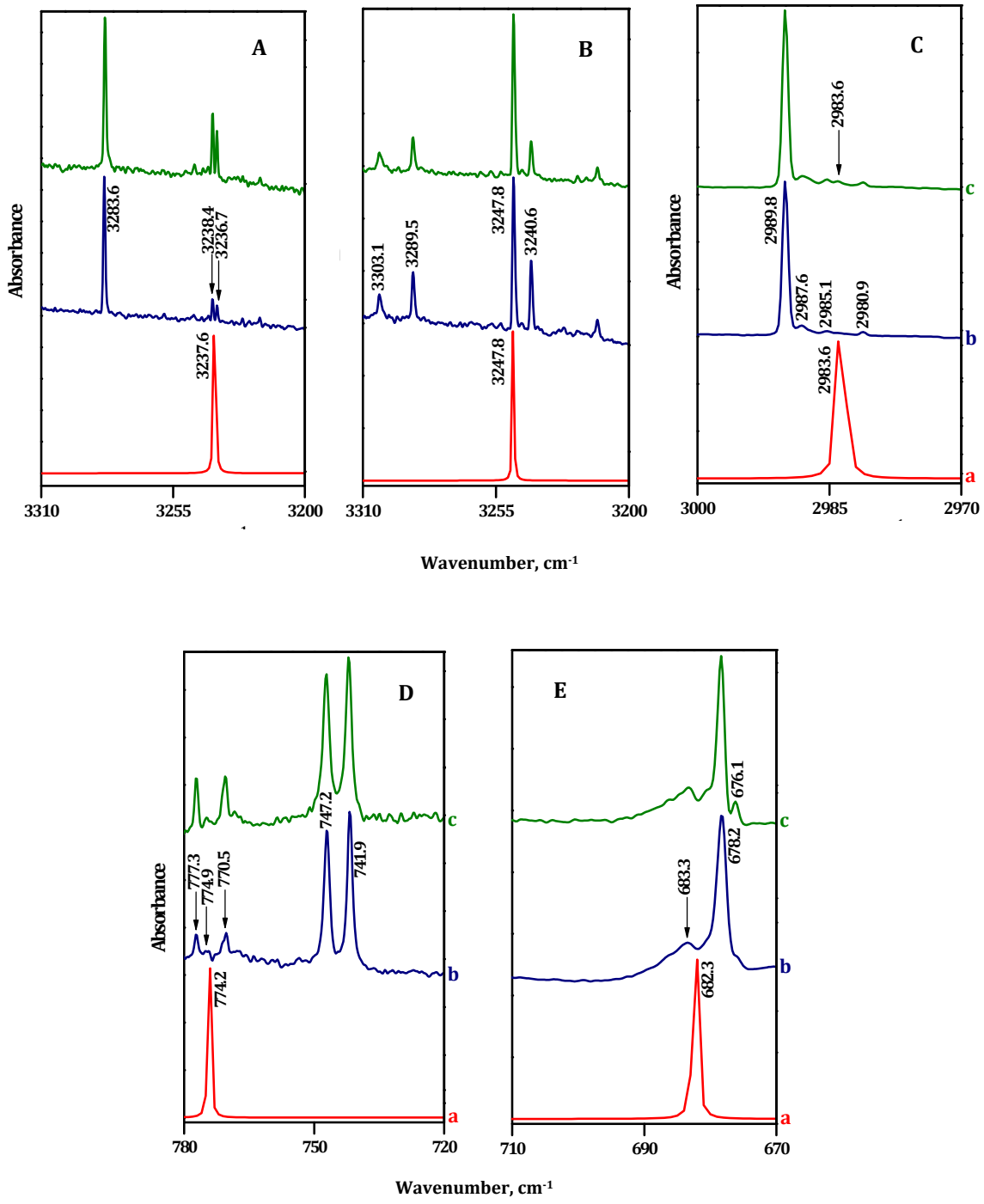

Figure S5. Grids 'A' and 'B' correspond to the infrared spectra of C-H stretching region of C_2H_2 in N2 and Ar matrixes respectively . Grid 'C' shows the infrared spectra of C-H stretching region of C_2H_4 in N_2 matrix; Grid 'D' shows the infrared spectra of C-H bending region of C_2H_2 in N_2 matrix. Grid 'E'corresponds to the infrared spectra of C-H bending region of C_6H_6 in N_2 matrix. Spectra are recorded at 12 K after annealing the matrix at 30 K(N_2) and 35 K (Ar). Trace 'a' in all grids correspond to computed scaled spectra and trace 'b' and 'c' correspond to variation of concentration of $POCl_3$ for the fixed concentration of π-donors.

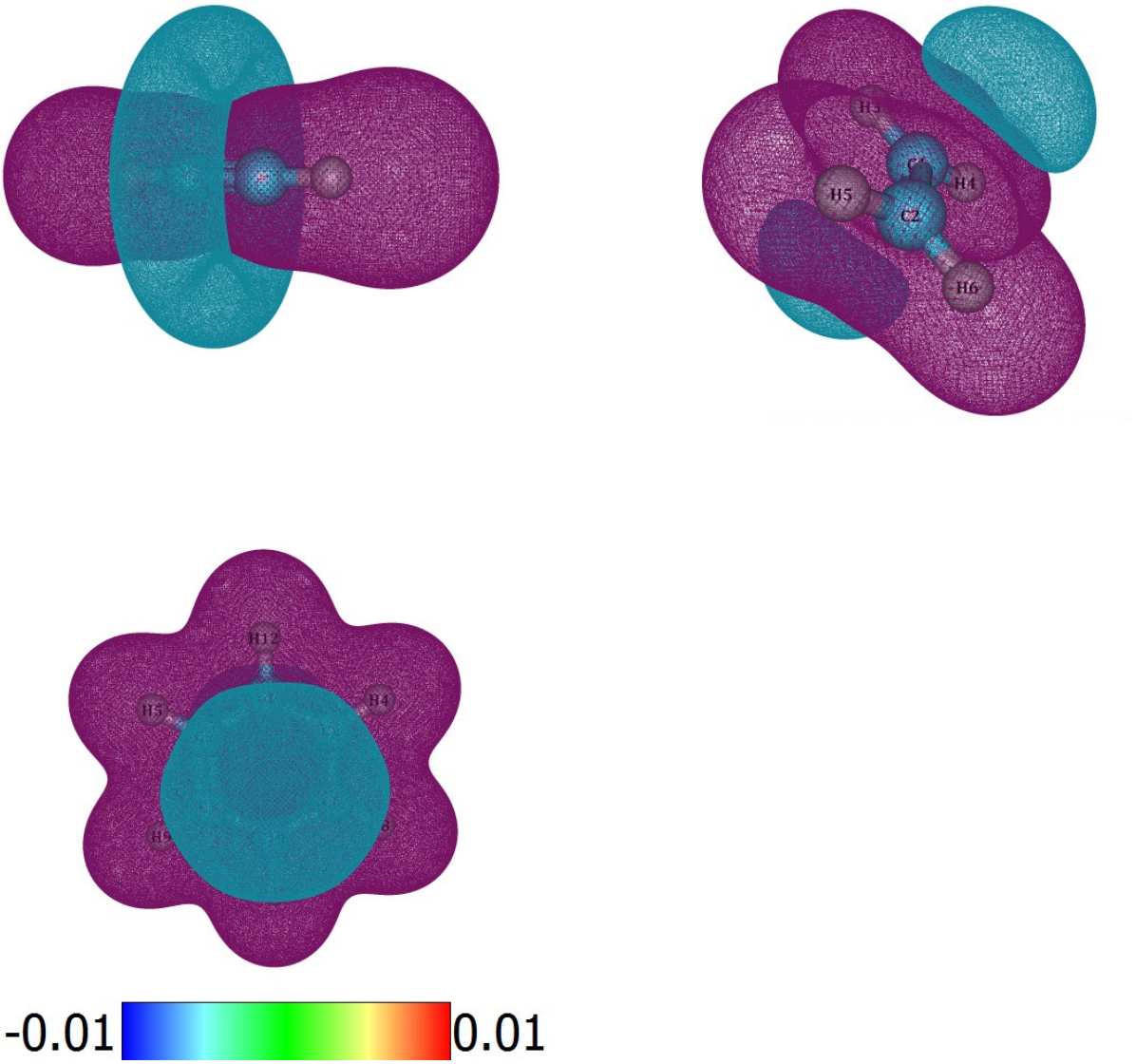

Figure S6. ESP mapping of C_2H_2, C_2H_4 and C_6H_6 using 0.01 au contour surface.

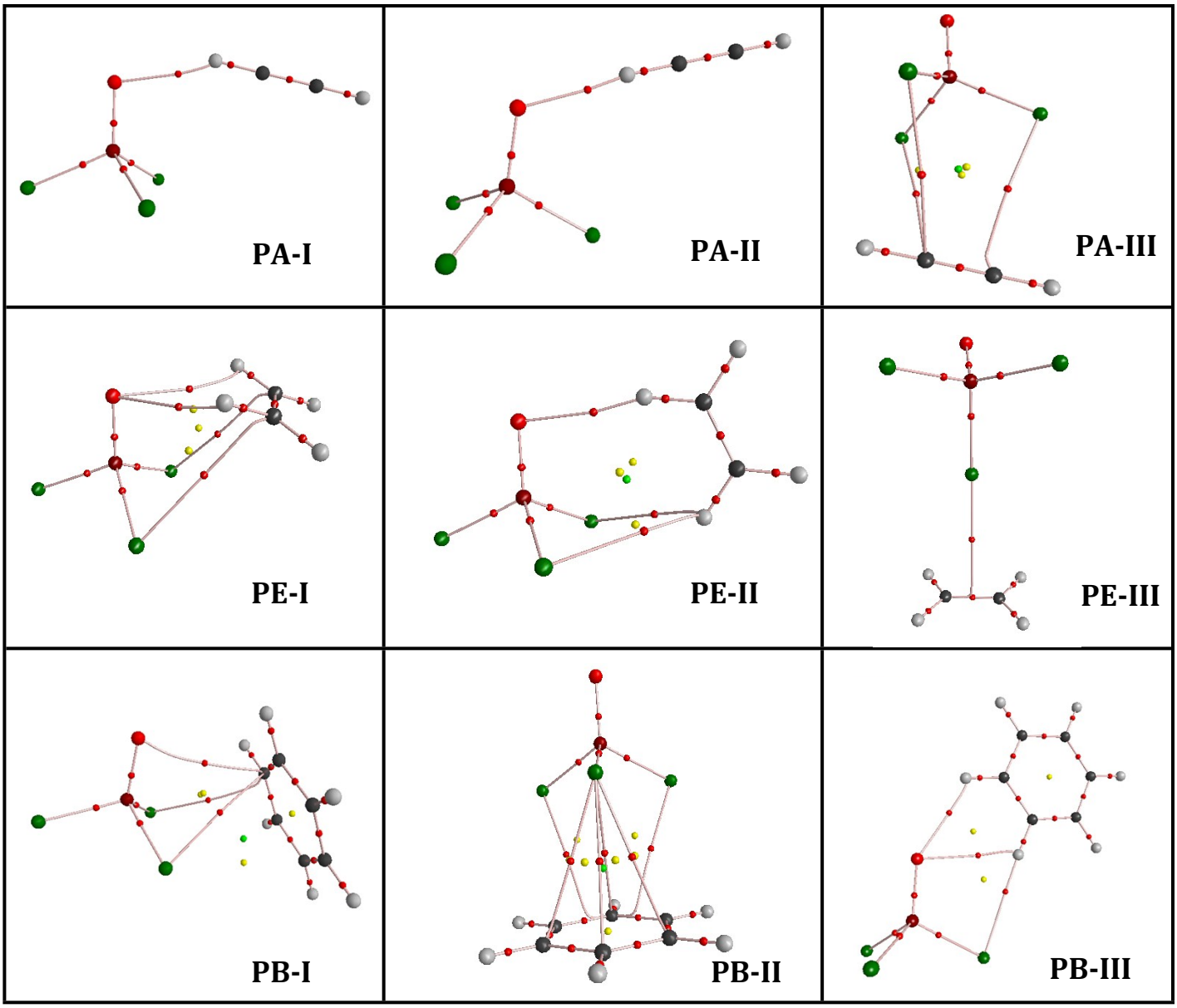

Figure S7. AIM Structures of all $POCl_3$-C_2H_2, $POCl_3$-C_2H_4 and $POCl_3$-C_6H_6 heterodimers.

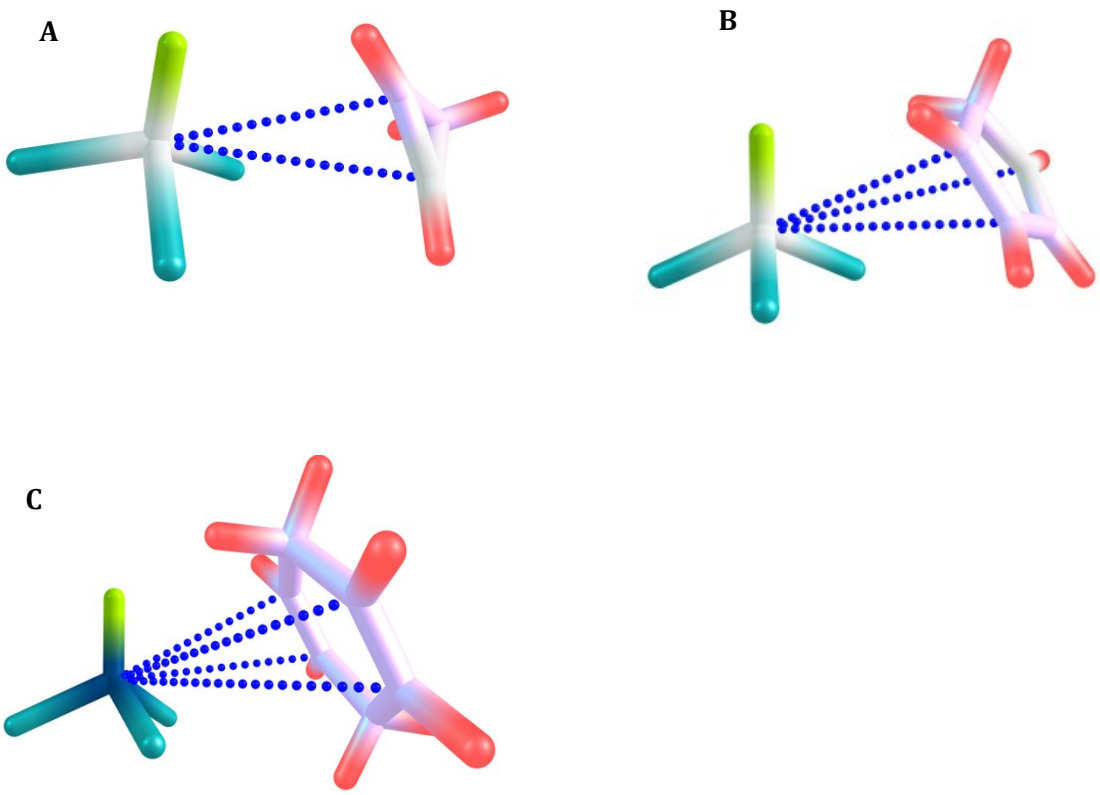

Figure S8. The structures of heterodimers of $POCl_3$ with non-aromatic π electron rich compounds computed at MP2/aug-cc-pVDZ level of theory; A) $POCl_3$: Cyclopropene B) $POCl_3$:1, 3-Cyclopentadiene C) $POCl_3$:1, 4-Cyclohexadiene

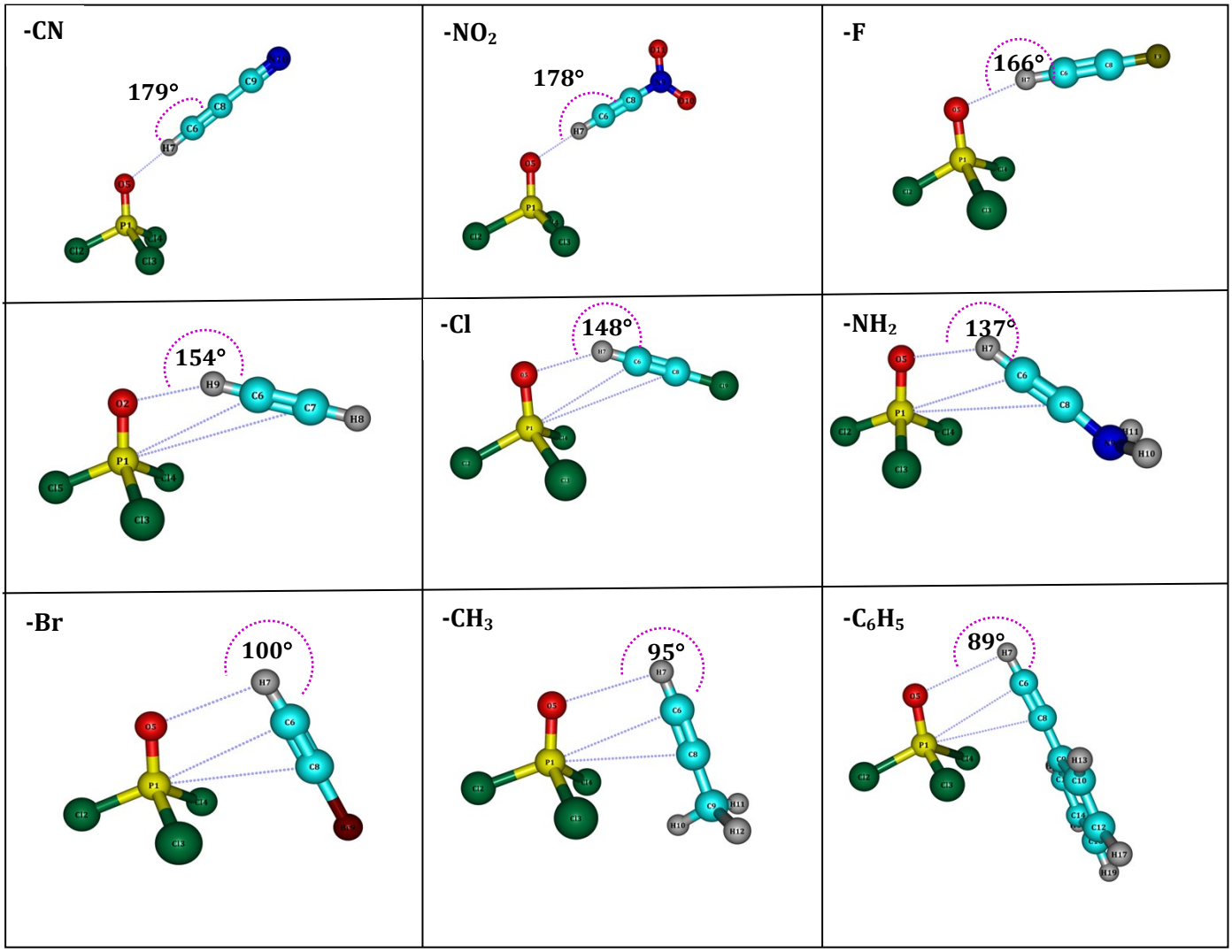

Figure S9. The structures of $POCl_3$ with substituted C_2H_2 heterodimers computed at MP2/aug-cc-pVDZ level of theory. The hydrogen bonding angle is shown alongside.

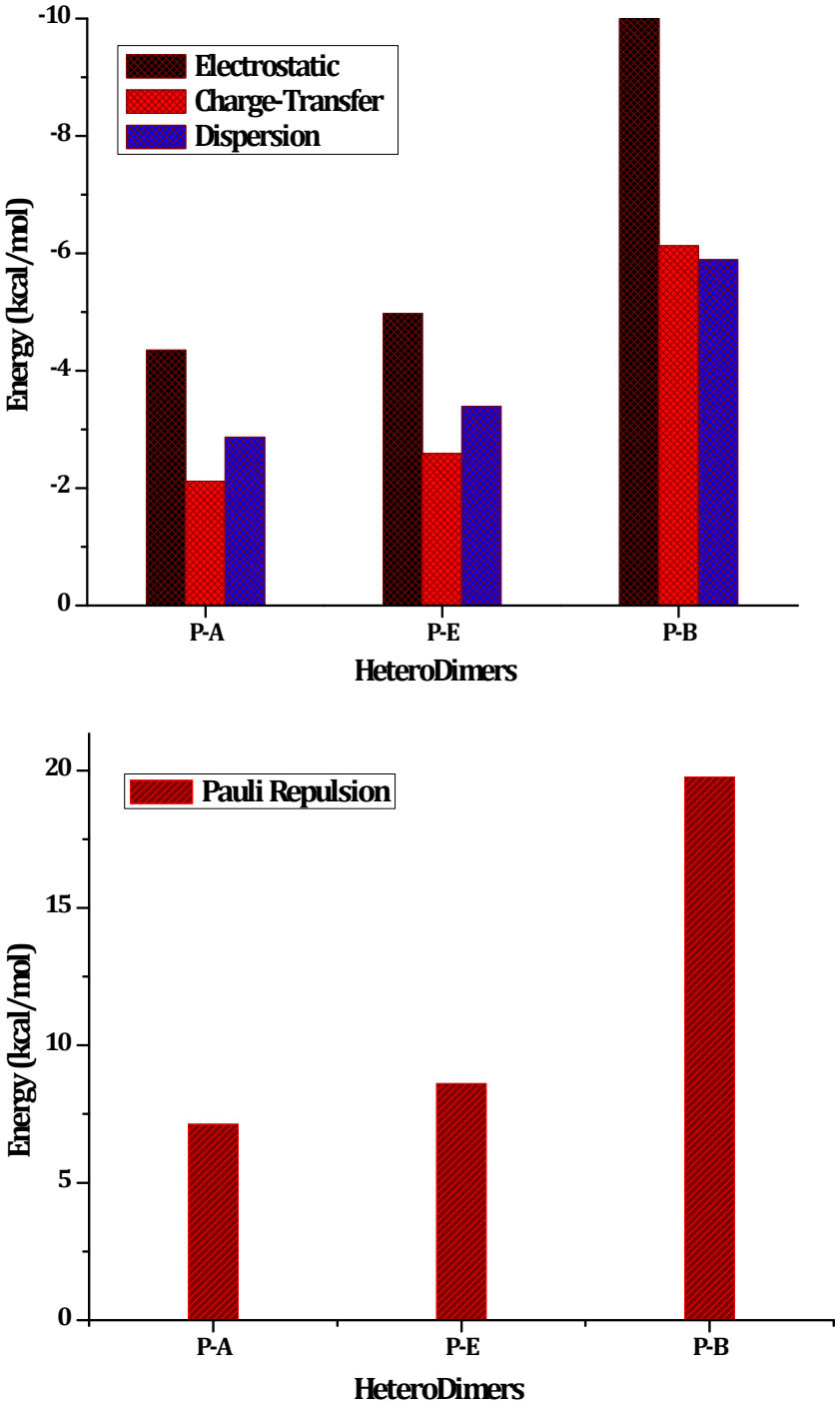

Figure S10. Bar Graph showing the different stabilizing and destabilizing interactions in PCl_3 heterodimers with C_2H_2 (P-A), C_2H_4 (P-E) and C_6H_6 (P-B).

Table S1. Computed and experimental vibrational wavenumbers, shifts in the wavenumbers and mode assignments for $POCl_3$–C_2H_2/C_2H_4/C_6H_6dimers calculated at the MP2 level of theory using aug-cc-pVDZ basis set.

Computed Wavenumber[a](cm^{-1})		**Experimental Wavenumber (cm^{-1})**				**Mode Assignment**
		N_2		**Ar**		
ν	**Δ ν**	**ν**	**Δ ν**	**ν**	**Δ ν**	
$POCl_3$						
1251.3(127)	-	1316.2/1313.5/ 1310.8[c]	-	1315.5/1314.2/ 1312.8[c]	-	$\nu_1$mode in $POCl_3$
C_2H_2						
3431.7(93)	-	3283.6	-	3289.5	-	ν_3 mode in C_2H_2
702.7(95) 702.7(95)	-	747.2/741.9[c]	-	737.1	-	ν_5 mode in C_2H_2
PA-I						
3400(183)	-31.1	3238.4/3236.7[c]	-46.0	3247.8	-41.7	ν_3 mode in C_2H_2
737.2(119) 740.21(83)	34.2 37.1	770.5 774.9/777.3[c]	25.9 29.6	-[b]	-	ν_5 mode in C_2H_2
1239.3(133)	-12.1	1307.9/1305.1[c]	-7.0	1307.5	-6.7	ν_1 mode in $POCl_3$
C_2H_4						
3175.6(11)	-	2989.8	-	2995.8	-	ν_{11} mode in C_2H_4
PE-I						
3172.6(8)	-3.0	2983.6	-6.2	-[b]	-	ν_{11} mode in C_2H_4
1248.2(124)	-3.1	1309.1/1306.9[c]	-5.5	1310.2	-4.0	ν_1 mode in $POCl_3$
C_6H_6						
678.3(116)	-	678.2	-	675.0	-	ν_4 mode in C_6H_6
PB-I						
679.3(124)	1.0	683.3	5.1	-[b]	-	ν_4 mode in C_6H_6
1246.9(102)	-4.5	1307.7/1306.2[c]	-6.6	1307.9/1309.8[c]	-5.3	ν_1 mode in $POCl_3$

[a]Intensities in km/mol given in parenthesis
[b]Features were not observed experimentally
[c]Average values are taken to compute the vibrational shifts

Table S2. Electron occupancies of various NBOs of $POCl_3$–C_2H_2/C_2H_4/C_6H_6 complexes computed at MP2/aug-cc-pVDZ level of theory. The important donor–acceptor delocalization interaction and delocalization energies (E_2) are also shown.

Complexes	NBO	Occupancy	Donor-Acceptor delocalization interaction	E_2 (kcal/mol)
$POCl_3$-C_2H_2 Heterodimers				
PA-I	n^1O2	1.97214(1.97348)[a]	$n^1O2 \rightarrow \sigma^*(C6\text{-}H9)$	1.19
	$\sigma^*(C6\text{-}H9)$	0.01086(0.00000)[b]		
	n^3O2	1.82487(1.81998)[a]	$n^3O2 \rightarrow \sigma^*(C6\text{-}H9)$	2.73
	$\sigma^*(C6\text{-}H9)$	0.01086(0.00000)[b]		
	n^3Cl3	1.98794(1.98853)[a]	$n^3Cl3 \rightarrow \pi^*(C6\text{-}C7)$	0.05
	$\pi^*(C6\text{-}C7)$	0.00966(0.00000)[b]		
	n^3Cl4	1.98794(1.98853)[a]	$n^3Cl4 \rightarrow \pi^*(C6\text{-}C7)$	0.05
	$\pi^*(C6\text{-}C7)$	0.00966(0.00000)[b]		
	$\sigma^*(P1\text{-}O2)$	0.10136(0.09868)[a]	$\sigma^*(P1\text{-}O2) \rightarrow \sigma^*(C6\text{-}H9)$	0.24
	$\sigma^*(C6\text{-}H9)$	0.01086(0.00521)[b]		
	$\sigma^*(P1\text{-}Cl5)$	0.16991(0.17462)[a]	$\sigma^*(P1\text{-}Cl5) \rightarrow \pi^*(C6\text{-}C7)$	0.14
	$\pi^*(C6\text{-}C7)$	0.00033(0.00000)[b]		
	π (C6-C7)	1.99862(1.99980)[b]	π (C6-C7)$\rightarrow\sigma^*(P1\text{-}Cl5)$	0.07
	$\sigma^*(P1\text{-}Cl5)$	0.16991(0.17462)[a]		
PA-II	n^1O2	1.97084(1.97348)[a]	$n^1O2 \rightarrow \sigma^*(C6\text{-}H9)$	2.27
	$\sigma^*(C6\text{-}H9)$	0.01229(0.00000)[b]		
	n^3O2	1.82587(1.81998)[a]	$n^3O2 \rightarrow \sigma^*(C6\text{-}H9)$	2.95
	$\sigma^*(C6\text{-}H9)$	0.01229(0.00000)[b]		
	n^2Cl5	1.95236(1.95547)[a]	$n^2Cl5 \rightarrow \pi^*(C6\text{-}C7)$	0.19
	$\pi^*(C6\text{-}C7)$	0.00961(0.00000)[b]		
	$\sigma^*(P1\text{-}O2)$	0.10095(0.09868)[a]	$\sigma^*(P1\text{-}O2) \rightarrow \sigma^*(C6\text{-}H9)$	0.35
	$\sigma^*(C6\text{-}H9)$	0.01229(0.00000)[b]		
PA-III	n^1Cl3	1.95416(1.95547)[a]	$n^2Cl3 \rightarrow \pi^*(C6\text{-}C7)$	0.09
	$\pi^*(C6\text{-}C7)$	0.00891(0.00000)[b]		
	n^2Cl3	1.95416(1.95547)[a]	$n^2Cl3 \rightarrow \sigma^*(C6\text{-}C7)$	0.13
	$\sigma^*(C6\text{-}C7)$	0.00075(0.00000)[b]		
	n^2Cl3	1.95416(1.95547)[a]	$n^2Cl3 \rightarrow \pi^*(C6\text{-}C7)$	0.33
	$\pi^*(C6\text{-}C7)$	0.00891(0.00000)[b]		
	n^3Cl3	1.95317(1.95358)[a]	$n^3Cl3 \rightarrow \pi^*(C6\text{-}C7)$	0.08
	$\pi^*(C6\text{-}C7)$	0.00891(0.00000)[b]		
	n^1Cl4	1.98828(1.98853)[a]	$n^1Cl4 \rightarrow \pi^*(C6\text{-}C7)$	0.09
	$\pi^*(C6\text{-}C7)$	0.00891(0.00000)[b]		
	n^2Cl4	1.95416(1.95547)[a]	$n^2Cl4 \rightarrow \sigma^*(C6\text{-}C7)$	0.13
	$\sigma^*(C6\text{-}C7)$	0.00075(0.00000)[b]		
	n^2Cl4	1.95416(1.95547)[a]	$n^2Cl4 \rightarrow \pi^*(C6\text{-}C7)$	0.33
	$\pi^*(C6\text{-}C7)$	0.00891(0.00000)[b]		
	n^3Cl4	1.95317(1.95358)[a]	$n^3Cl4 \rightarrow \pi^*(C6\text{-}C7)$	0.08
	$\pi^*(C6\text{-}C7)$	0.00891(0.00000)[b]		
	n^1Cl5	1.98834(1.98853)[a]	$n^1Cl5 \rightarrow \pi^*(C6\text{-}C7)$	0.06
	$\pi^*(C6\text{-}C7)$	0.00891(0.00000)[b]		
	n^2Cl5	1.95427(1.95547)[a]	$n^2Cl5 \rightarrow \pi^*(C6\text{-}C7)$	0.22
	$\pi^*(C6\text{-}C7)$	0.00891(0.00000)[b]		
	π C6-C7	1.99886(1.99980)[b]	π C6-C7$\rightarrow\sigma^*(P1\text{-}O2)$	0.08
	$\sigma^*(P1\text{-}O2)$	0.09787(0.09868)[a]		

Complexes	NBO	Occupancy	Donor-Acceptor delocalization interaction	E_2 (kcal/mol)
$POCl_3$-C_2H_4 Heterodimers				
PE-I	n^2O2	1.82359(1.81998)[a]	$n^2O2 \rightarrow \sigma^*$(C6-H8)	0.09
	σ*(C6-H8)	0.00853(0.00820)[b]		
	n^2O2	1.82359(1.81998)[a]	$n^2O2 \rightarrow \sigma^*$(C6-H9)	0.17
	σ*(C6-H9)	0.00849(0.00820)[b]		
	n^2O2	1.82359(1.81998)[a]	$n^2O2 \rightarrow \sigma^*$(C7-H10)	0.09
	σ*(C7-H10)	0.00853(0.00820)[b]		
	n^2O2	1.82359(1.81998)[a]	$n^2O2 \rightarrow \sigma^*$(C7-H11)	0.17
	σ*(C7-H11)	0.00849(0.00820)[b]		
	n^3O2	1.82120(1.81998)[a]	$n^3O2 \rightarrow \sigma^*$(C6-H9)	0.09
	σ*(C6-H9)	0.00849(0.00820)[b]		
	n^3O2	1.82120(1.81998)[a]	$n^3O2 \rightarrow \sigma^*$(C7-H11)	0.09
	σ*(C7-H11)	0.00849(0.00820)[b]		
	n^2Cl3	1.95396(1.95547)[a]	$n^2Cl3 \rightarrow \sigma^*$(C6-C7)	0.22
	σ*(C6-C7)	0.00223(0.00000)[b]		
	n^3Cl3	1.95224(1.95358)[a]	$n^3Cl3 \rightarrow \sigma^*$(C6-C7)	0.22
	σ*(C6-C7)	0.00223(0.00000)[b]		
	n^2Cl4	1.95396(1.98853)[a]	$n^2Cl4 \rightarrow \sigma^*$(C6-C7)	0.22
	σ*(C6-C7)	0.00223(0.00000)[b]		
	n^3Cl4	1.95224(1.95547)[a]	$n^3Cl4 \rightarrow \sigma^*$(C6-C7)	0.22
	σ*(C6-C7)	0.00223(0.00000)[b]		
	σ(C6-C7)	1.99732(1.99934)[b]	σ(C6-C7)→ σ*(P1-O2)	0.10
	σ*(P1-O2)	0.09961(0.09868)[a]		
	σ(C6-C7)	1.99732(1.99934)[b]	σ(C6-C7)→ σ*(P1-Cl5)	0.39
	σ*(P1-Cl5)	0.17202(0.17462)[a]		
	π(C6-C7)	1.99165(1.99235)[b]	π_2(C6-C7)→ σ*(P1-O2)	0.07
	σ*(P1-O2)	0.09961(0.09868)[b]		
PE-II	n^2O2	1.82209(1.81998)[a]	$n^2O2 \rightarrow \sigma^*$(C6-H8)	0.28
	σ*(C6-H8)	0.01018(0.00820)[b]		
	n^3O2	1.82067(1.81998)[a]	$n^2O2 \rightarrow \sigma^*$(C6-H9)	1.39
	σ*(C6-H8)	0.01018(0.00820)[b]		
	n^3Cl4	1.95128(1.98853)[a]	$n^3Cl4 \rightarrow \sigma^*$(C7-H10)	0.41
	σ*(C7-H10)	0.00977(0.00820)[b]		
	n^3Cl5	1.95127(1.95358)[a]	$n^3Cl5 \rightarrow \sigma^*$(C7-H10)	0.41
	σ*(C7-H10)	0.00977(0.00820)[b]		
	σ*(P1-Cl3)	0.17242(0.17462)[a]	σ*(P1-Cl3)→ σ*(C6-H8)	0.07
	σ*(C6-H8)	0.01018(0.00820)[b]		
PE-III	n^2Cl3	1.95128 (1.95547)[a]	$n^2Cl3 \rightarrow \sigma^*$(C6-C7)	0.27
	σ*(C6-C7)	0.00104 (0.00000)[b]		
	n^2Cl3	1.95128 (1.95547)[a]	$n^2Cl3 \rightarrow \pi^*$(C6-C7)	0.05
	π*(C6-C7)	0.00227(0.00246) [b]		
	σ(C6-C7)	1.99429 (0.17462)[a]	σ(C6-C7)→σ*(P1-Cl3)	0.79
	σ*(P1-Cl3)	0.17173(0.17462)[a]		
	π(C6-C7)	1.99277 (1.99235)[b]	π(C6-C7)→σ*(P1-Cl3)	0.17
	σ*(P1-Cl3)	0.17173 (0.17462)[a]		

Complexes	NBO	Occupancy	Donor-Acceptor delocalization interaction	E_2 (kcal/mol)
$POCl_3$-C_6H_6 Heterodimers				
PB-I	n^2O2	1.82409(1.81998)[a]	$n^2O2 \rightarrow \sigma^*(C6-C7)$	0.08
	$\sigma^*(C6-C7)$	0.01414(0.01389)[b]		
	n^2O2	1.82409(1.81998)[a]	$n^2O2 \rightarrow \pi^*(C6-C7)$	0.22
	$\pi^*(C6-C7)$	0.33274(0.33237)[b]		
	n^2O2	1.82409(1.81998)[a]	$n^2O2 \rightarrow \sigma^*(C11-C15)$	0.07
	$\sigma^*(C11-C15)$	0.01385(0.01389)[b]		
	n^2O2	1.82409(1.81998)[a]	$n^2O2 \rightarrow \pi^*(C11-C15)$	0.28
	$\pi^*(C11-C15)$	0.32093(0.33237)[b]		
	$\pi(C6-C7)$	1.66862(1.66397)[b]	$\pi(C6-C7) \rightarrow \sigma^*(P1-O2)$	0.08
	$\sigma^*(P1-O2)$	0.10015(0.09868)[a]		
	$\pi(C6-C7)$	1.66862(1.66397[b]	$\pi(C6-C7) \rightarrow \sigma^*(P1-Cl4)$	0.07
	$\sigma^*(P1-Cl4)$	0.17663(0.17462)[a]		
	$\pi(C6-C7)$	1.66862(1.66397)[b]	$\pi(C6-C7) \rightarrow \sigma^*(P1-Cl5)$	0.60
	$\sigma^*(P1-Cl5)$	0.17419(0.17462)[a]		
	$\pi(C8-C12)$	1.67107(1.66397)[b]	$\pi(C8-C12) \rightarrow \sigma^*(P1-Cl3)$	0.07
	$\sigma^*(P1-Cl3)$	0.16903(0.17462)[a]		
	$\pi(C6-C7)$	1.66862(1.66397)[b]	$\pi(C6-C7) \rightarrow \sigma^*(P1-O2)$	0.24
	$\sigma^*(P1-O2)$	0.10015(0.09868)[a]		
	$\pi(C8-C12)$	1.67107(1.66397)[b]	$\pi(C8-C12) \rightarrow \sigma^*(P1-Cl3)$	0.25
	$\sigma^*(P1-Cl3)$	0.16903(0.17462)[a]		
	$\pi(C11-C15)$	1.65774(1.66397)[b]	$\pi(C11-C15) \rightarrow \sigma^*(P1-O2)$	0.09
	$\sigma^*(P1-O2)$	0.10015(0.09868)[a]		
PB-II	n^2Cl3	1.95555(1.95547)[a]	$n^2Cl3 \rightarrow \sigma^*(C12-C15)$	0.06
	$\sigma^*(C12-C15)$	0.01410(0.01389)[b]		
	n^3Cl3	1.95437(1.95358)[a]	$n^3Cl3 \rightarrow \pi^*(C8-C12)$	0.09
	$\pi^*(C8-C12)$	0.33277(0.33237)[b]		
	n^2Cl4	1.95556(1.95547)[a]	$n^2Cl4 \rightarrow \sigma^*(C8-C12)$	0.06
	$\sigma^*(C8-C12)$	0.01410(0.01389)[b]		
	n^2Cl4	1.95556(1.95547)[a]	$n^2Cl4 \rightarrow \pi^*(C8-C12)$	0.24
	$\pi^*(C8-C12)$	0.33277(0.33237)[b]		
	n^2Cl4	1.95556(1.95547)[a]	$n^2Cl4 \rightarrow \pi^*(C11-C15)$	0.21
	$\pi^*(C11-C15)$	0.01401(0.33237)[b]		
	n^3Cl4	1.95438(1.95358)[a]	$n^3Cl4 \rightarrow \pi^*(C11-C15)$	0.10
	$\pi^*(C11-C15)$	0.33111(0.33237)[b]		
	n^3Cl5	1.94930(1.95358)[a]	$n^3Cl5 \rightarrow \pi^*(C6-C7)$	0.05
	$\pi^*(C6-C7)$	0.33413(0.33237)[b]		
	$\pi(C6-C7)$	1.66446(1.66397)[b]	$\pi(C6-C7) \rightarrow \sigma^*(P1-Cl5)$	0.22
	$\sigma^*(P1-Cl5)$	0.16865(0.17462)[a]		
	$\pi(C8-C12)$	1.66304(1.66397)[b]	$\pi(C8-C12) \rightarrow \sigma^*(P1-O2)$	0.13
	$\sigma^*(P1-O2)$	0.09823(0.09868)[a]		
	$\pi^*(C6-C7)$	0.33413(0.33237)[b]	$\pi^*(C6-C7) \rightarrow \sigma^*(P1-Cl5)$	0.32
	$\sigma^*(P1-Cl5)$	0.16865(0.17462)[a]		
	$\pi^*(C8-C12)$	0.33277(0.33237)[b]	$\pi^*(C8-C12) \rightarrow \sigma^*(P1-O2)$	0.07
	$\sigma^*(P1-O2)$	0.09823(0.09868)[a]		
	$\pi^*(C8-C12)$	0.33277(0.33237)[b]	$\pi^*(C8-C12) \rightarrow \sigma^*(P1-Cl5)$	0.09
	$\sigma^*(P1-Cl5)$	0.16865(0.17462)[a]		
	$\pi^*(C11-C15)$	0.33111(0.33237)[b]	$\pi^*(C11-C15) \rightarrow \sigma^*(P1-Cl5)$	0.45

	σ*(P1-Cl5)	0.16865(0.17462)[a]		
PB-III	n^1Cl2	1.98813(1.98853)[a]	n^2Cl2→ σ*(C8-H13)	0.19
	σ*(C8-H13)	0.01316(1.98451)[b]		
	n^3Cl2	1.95269(1.95547)[a]	n^3Cl2→ σ*(C8-H13)	1.62
	σ*(C8-H13)	0.01316(1.98451)[b]		
	n^1O5	1.97211(1.97348)[a]	n^1O5→ σ*(C6-C7)	0.12
	σ*(C6-C7)	0.01381(0.33237)[b]		
	n^1O5	1.97211(1.97348)[a]	n^1O5→ σ*(C6-H9)	0.76
	σ*(C6-H9)	0.01042(1.98451)[b]		
	n^3O5	1.82192(1.81998)[a]	n^2Cl4→ σ*(C11-C15)	0.09
	σ*(C6-C7)	0.01381(0.33237)[b]		
	n^3O5	1.82192(1.81998)[a]	n^3O5→ σ*(C6-H9)	0.07
	σ*(C6-H9)	0.01042(1.98451)[b]		
	n^3O5	1.82192(1.81998)[a]	n^3O5→ σ*(C8-C12)	0.08
	σ*C8-C12)	0.01408(0.33237)[b]		
	n^3O5	1.82192(1.81998)[a]	n^3O5→ σ*(C8-H13)	0.26
	σ*(C8-H13)	0.01316(1.98451)[b]		
	σ (C6-C8)	1.97816(0.33237)[b]	σ (C6-C8)→ σ*(P1-O5)	0.07
	σ*(P1-O5)	0.09916(0.09868)[a]		

[a]Occupancy of monomeric $POCl_3$ is given in parentheses.
[b]Occupancy of monomeric $C_2H_2/C_2H_4/C_2H_6$ is given in parentheses.

Table S3. The properties of (3,-1) bond critical points (BCP) of various heterodimers. The BCPs of the monomers are given in parenthesis.

Heterodimers	$\rho(r_c)^a$	$\Delta^2 \rho(r_c)^a$	$\lambda_1{}^a$	$\lambda_2{}^a$	$\lambda_3{}^a$
PA-I					
O2···H9	0.01344	-0.01025	-0.01360	-0.01284	0.06742
P1-O2	0.20204(0.20313)	-0.37256(-0.37754)	-0.32322(-0.32412)	-0.32316(-0.32412)	2.13664(2.15841)
C6-H9	0.27497(0.27608)	0.27922(0.27659)	-0.72496(-0.71725)	-0.72448(-0.71725)	0.33255(0.32815)
C6-C7	0.37026(0.37003)	0.216620(0.21497)	-0.55040(-0.54464)	-0.55018(-0.54464)	0.23394(0.22941)
PA-II					
O2···H9	0.01463	-0.01173	-0.01551	-0.01536	0.07778
P1-O2	0.20206(0.20313)	-0.37323(-0.37754)	-0.32392(-0.32412)	-0.32350(-0.32412)	2.14034(2.15841)
C6-H9	0.27474(0.27608)	0.27897(0.27659)	-0.72569(-0.71725)	-0.72557(-0.71725)	0.33538(0.32815)
C6-C7	0.37048(0.37003)	0.21693(0.21497)	-0.55148(-0.54464)	-0.55133(-0.54464)	0.23509(0.22941)
PA-III					
Cl3···C7	0.00536	-0.00373	-0.00292	-0.00225	0.02011
Cl4···C7	0.00536	-0.00373	-0.00292	-0.00225	0.02011
Cl5···C6	0.00467	-0.00295	-0.00245	-0.00191	0.01617
C6-C7	0.36969(0.37003)	0.21479(0.21497)	-0.54519(-0.54464)	-0.54422(-0.54464)	0.23026(0.22941)
PE-I					
O2···H11	0.00643	-0.00599	-0.00478	-0.00284	0.03160
O2···H9	0.00643	-0.00600	-0.00479	-0.00285	0.06316
P1-O2	0.20281(0.20313)	-0.37642(-0.37754)	-0.32409(-0.32412)	-0.32363(-0.32412)	2.15341(2.15841)
Cl4···C7	0.00548	-0.00386	-0.00253	-0.00169	0.01964
Cl3···C6	0.00548	-0.00386	-0.00253	-0.00169	0.01967
C6-C7	0.32418(0.32462)	0.20038(0.20080)	-0.66736(-0.66939)	-0.49651(-0.49653)	0.36233(0.36272)
C7-H11	0.27403(0.27307)	0.25316(0.24989)	-0.68897(-0.68234)	-0.67906(-0.67293)	0.35541(0.35570)
C6-H9	0.27403(0.27307)	0.25315(0.24989)	-0.68896(-0.68234)	-0.67905(-0.67293)	0.35541(0.35570)
P1-Cl4	0.12818(0.12759)	0.00874(0.00945)	-0.13691(-0.13558)	-0.13452(-0.13339)	0.23649(0.23116)
P1-Cl3	0.12818(0.12759)	0.00872(0.00945)	-0.13692(-0.13558)	-0.13453(-0.13339)	0.23653(0.23116)
PE-II					
O2···H8	0.00902	-0.00685	-0.00832	-0.00792	0.04364
Cl5···H10	0.00493	-0.00406	-0.00348	-0.00299	0.02271
Cl4···H10	0.00493	-0.00406	-0.00347	-0.00299	0.02268
P1-O2	0.02293(0.20313)	-0.37630(-0.37754)	-0.32421(-0.32412)	-0.32420(-0.32412)	2.15361(2.15841)
C6-H8	0.27428(0.27307)	0.25443(0.24989)	-0.69061(-0.68234)	-0.68198(-0.67293)	0.35488(0.35570)
C7-H10	0.27295(0.27307)	0.24829(0.24989)	-0.68037(-0.68234)	-0.67095(-0.67293)	0.38514(0.35570)
P1-Cl5	0.12803(0.12759)	0.00851(0.00945)	-0.13634(-0.13558)	-0.13422(-0.13339)	0.23651(0.23116)
P1-Cl4	0.12803(0.12759)	0.00853(0.00945)	-0.13633(-0.13558)	-0.13422(-0.13339)	0.23643(0.23116)

PE-III					
Cl3···C6	0.00796	-0.00543	-0.00473	-0.00279	0.02923
Cl3···C7	0.00796	-0.00543	-0.00473	-0.00279	0.02923
C6-C7	0.32403(0.32462)	0.20023(0.20080)	-0.66726(-0.66939)	-0.49642(-0.49653)	0.36276(0.36272)
P1-Cl3	0.12930(0.12759)	0.01066(0.00945)	-0.13837(-0.13558)	-0.13579(-0.13339)	0.23152(0.23116)
PB-I					
O2···C7	0.00747	-0.00576	-0.00336	-0.00191	0.02832
Cl4···C7	0.00613	-0.00402	-0.00251	-0.00128	0.01988
Cl3···C7	0.00736	-0.00515	-0.00321	-0.00059	0.02442
C6-C7	0.29105(0.29544)	0.17412(0.17450)	-0.58336(-0.58485)	-0.48624(0.48768)	0.37310(0.37445)
P1-O2	0.20271(0.20313)	-0.37592(-0.37754)	-0.32401(-0.32412)	-0.32337(-0.32412)	2.15105(2.15841)
P1-Cl4	0.12684(0.12759)	-0.01005(0.00945)	-0.13444(-0.13558)	-0.13241(-0.13339)	0.22664(0.23116)
P1-Cl3	0.12983(0.12759)	0.00679(0.00945)	-0.13933(-0.13558)	-0.13687(-0.13339)	0.24901(0.23116)
PB-II					
Cl5···C7	0.00696	-0.00527	-0.00353	-0.00018	0.02483
Cl5···C11	0.00698	-0.00527	-0.00345	-0.00017	0.02474
Cl5···C6	0.00698	-0.00527	-0.00345	-0.00017	0.02471
Cl5···C12	0.00713	-0.00509	-0.00358	-0.00043	0.02344
Cl3···C12	0.00587	-0.00378	-0.00303	-0.00113	0.01926
Cl4···C12	0.00587	-0.00378	-0.00303	-0.00113	0.01926
C6-C7	0.29506(0.29544)	0.17429(0.17450)	-0.58356(-0.58485)	-0.48717(0.48768)	0.37358(0.37445)
C11···C7	0.29506	0.17429	-0.58356	-0.48717	0.37358
P1-Cl5	0.12980(0.12759)	0.00665(0.00945)	-0.13923(-0.32412)	-0.13634(-0.13339)	0.24897(0.23116)
P1-Cl4	0.12645(0.12759)	0.01006(0.00945)	-0.13365(-0.32412)	-0.13149(-0.13339)	0.22491(0.23116)
P1-Cl3	0.12646(0.12759)	0.01004(0.00945)	-0.13365(-0.32412)	-0.13149(-0.13339)	0.22497(0.23116)
PB-III					
O5···H9	0.00823	-0.00768	-0.00757	-0.00702	0.04532
O5···H13	0.00667	-0.00611	-0.00551	-0.00445	0.03440
Cl3···H13	0.00718	-0.00575	-0.00559	-0.00557	0.03417
P1-Cl3	0.12744(0.12759)	0.00896(0.00945)	-0.13525(-0.32412)	-0.13339(-0.13339)	0.23281(0.23116)
P1-O5	0.20286(0.20313)	-0.37691(-0.37754)	-0.32459(-0.32412)	-0.32348(-0.32412)	2.15571(2.15841)
C6-H9	0.27512(0.27301)	0.25594(0.24926)	-0.69731(0.68406)	-0.68803(-0.67422)	0.36156(0.36126)
C8-H13	0.27463(0.27301)	0.25213(0.24926)	-0.69148(0.68406)	-0.68181(-0.67422)	0.36477(0.36126)

Table S4. Proton affinity of C_2H_2, C_2H_4, C_6H_6 and substituted C_2H_2 calculated at MP2 level of theory with aug-cc-pVDZ basis set.

Structures	**Proton affinity (kcal/mol)**
C_2H_2	-149.9
C_2H-CN	-129.8
C_2H-NO_2	-148.1
C_2H-F	-154.1
C_2H-Cl	-161.6
C_2H-Br	-163.6
C_2H-CH_3	-168.0
C_2H-C_6H_6	-190.8
C_2H-NH_2	*-206.2*
C_2H_4	-160.3
C_6H_6	-313.3