Table 1. Electronic structure of adsorbed orthocarborane (1,2-$C_2B_{10}H_{12}$). The comparison of the semi-empirical ground state theory of the molecular orbitals (PM3-NDO and MNDO), for a single orthocarborane, with experiment. All energies are in eV. {†}refers to reference [1], {§} refers to reference [2] and {#} refers to reference [3].

symmetry representation	theory: MNDO	theory: PM3	Cu	Ag	Co
$12a_1$	-0.11§	0.288			
$8b_1$	-0.41§	0.157			
$9b_2$	-0.43§	-0.113	5.6§		3.4#
$7b_2$	-0.7§	-0.368			
$11a_1$	-0.93§	-0.679			
$7b_1$ (LUMO)	-1.21§	-0.696			
$6b_2$ (HOMO)	-12.18§, -12.18†	-10.778			
$6b_1$	-12.2§, -12.20†	-10.874	-5.7§	-5.9	-4.9#
$3a_2$	-12.36§, -12.37†	-10.998			
$10a_1$	-12.37§, -12.71†	-11.042			
$9a_1$	-12.71§, -12.86†	-11.364			
$5b_2$	-12.93§, -12.93†	-11.435			
$5b_1$	-13.15§, -13.15†	-11.440			
$2a_2$	-13.23§, -13.24†	-12.038			
$8a_1$	-13.68§, -13.68†	-13.138	-6.7§		
$4b_1$	-15.1§, -15.10†	-14.015			
$4b_2$	-15.4§, -15.43†	-14.034	-8.5§	-8.9	-7.5#
$7a_1$	-15.43§, -15.43†	-14.540			
$3b_1$	-16.25§, -16.26†	-14.687			
$6a_1$	-16.57§, -16.56†	-15.111	-11.4§	-11.5	
$3b_2$	-17.1§, -17.07†	-15.330			
$5a_2$	-18.96§		-12.5		

Table 2. Electronic structure of adsorbed metacarborane (1,7-$C_2B_{10}H_{12}$). The comparison of the semi-empirical ground state theory (PM3-NDO and MNDO) of the molecular orbitals of a single orthocarborane with experiment. All energies are in eV. {†}refers to reference [1], and {#} refers to reference [3].

symmetry representation	theory: MNDO	theory: PM3	Ag	Au	Co
	1.19#	1.557			
	1#	1.110			
	0.8#	1.007			
$9b_1$	0.7#	0.685		4.7	
$8b_1$	0.54#	0.681			
$9b_2$	0.27#	0.500			
$4a_2$	-0.08#	0.190			
$12a_1$	-0.22#	0.163			
$8b_2$	-0.26#	0.154			
$11a_1$	-0.58#	-0.426		3.2	2.5#
$7b_1$	-1#	-0.641			
$7b_2$ (LUMO)	-1.25#	-0.678			
$10a_1$ (HOMO)	-12.12#, -12.12†	-10.717			
$3a_2$	-12.27#, -12.27†	-10.831	-6.4	-5.8	-5.6#
$6b_2$	-12.45#, -12.46†	-10.986			
$6b_1$	-12.67#, -12.64†	-11.326			
$9a_1$	-12.77#, -12.76†	-11.365			
$5b_2$	-12.93#, -12.91†	-11.814			
$8a_1$	-13.12#, -13.15†	-11.910	-6.9	-6.9	
$2a_2$	-13.41#, -13.40 †	-12.403			
$5b_1$	-13.51#, -13.40†	-12.497			
$7a_1$	-15.13#, -15.13†	-13.851			
$4b_2$	-15.16#, -15.15†	-13.967	-8.7	-8.8	-7.8#
$4b_1$	-15.54#, -15.55†	-14.547			
$3b_1$	-16.24#, -16.24†	-14.624	-9.3		
$3b_2$	-16.54#, -16.55†	-14.913			
$6a_1$	-16.97#, -16.96†	-15.340	-11.7	-11.6	
$5a_1$	-18.86#, -18.86†	-18.644	-16.3	-15.9	

Table 3. Electronic structure of adsorbed paracarborane (1,12-$C_2B_{10}H_{12}$). The comparison of the semi-empirical ground state theory (PM3-NDO and MNDO) of the molecular orbitals of a single paracarborane with experiment. All energies are in eV. {†} and refers to reference [4].

symmetry representation	theory: Gaussian,3-21G)	theory: PM3	Ag	Au
$7a_{1g}$		3.82559		
$4e_{2u}$		3.67172		
$4e_{2U}$		3.67138		
$6e_{1u}$		3.59679		
$6e_{1u}$		3.59542		
$1a_{1u}$		3.41784		
$6a_{2u}$		3.38797		5.35
$5a_{2u}$		3.15252		
$5e_{1u}$		2.97673		
$5e_{1u}$		2.97562		
$6a_{1g}$		2.62901		
$4e_{1u}$		2.43577		
$4e_{1u}$		2.43418		
$4e_{2g}$		1.693		
$4e_{2g}$		1.69203		
$5a_{1g}$		0.96332		
$4e_{1g}$		0.51974		
$4e_{1g}$		0.51645		
$3e_{2g}$		0.49789		
$3e_{2g}$		0.4971		1.5
$3e_{1g}$		0.02319		
$3e_{1g}$		0.02296		
$4a_{2u}$		-0.35775		
$3e_{2u}$		-0.63943		
$3e_{2u}$ (LUMO)	3.32†	-0.63999		
$2e_{2u}$ (HOMO)	-10.99†	-10.65521		
$2e_{2u}$		-10.65606		-8
$2e_{2g}$		-11.2579	-8.5	
$2e_{2g}$		-11.25819		-8.55
$2e_{1g}$		-11.94996	-9.8	-10.2
$2e_{1g}$		-11.95086		
$4a_{1g}$		-12.02213		
$3e_{1u}$		-12.16138		
$3e_{1u}$	-12.53†	-12.16623		
$2e_{1u}$	-13.09†	-13.80127		
$2e_{1u}$	-13.15†	-13.80167		
$1e_{2u}$	-13.35†	-14.51568	-13.4	-12.3
$1e_{2u}$	-15.06†	-14.51657		
$3a_{2u}$	-15.23†	-14.81571		
$2a_{2u}$	-15.84†	-15.84573		
$3a_{1g}$	-18.41†	-18.59202		
$1e_{2g}$	-19.68†	-19.06446		
$1e_{2g}$	-22.67†	-19.06659	-16.5	-15
$1e1_g$		-19.53194		
$1e_{1g}$		-19.53809		

Table 4. Electronic structure of adsorbed orthophosphacarborane (1,2-$PCB_{10}H_{12}$). The comparison of the semi-empirical ground state theory (PM3-NDO) of the molecular orbitals of a single orthophosphacarborane with experiment. All energies are in eV.

theory (PM3)	Ag	Au
1.343	4.9	5.2
0.796		
0.669		
0.241		
0.176	3	
-0.049		
-0.064		
-0.854		
-1.087		
-1.265	1.9	2.4
-1.370		
-1.958 (LUMO)		
-10.228 (HOMO)	-6.1	-5.6
-10.866		
-10.943		
-11.025		
-11.166	-7.3	-7.1
-11.169		
-11.415		
-12.050		
-12.178	-9.2	-8.3
-12.916		
-13.707		
-14.307		
-14.729	-12	-11.3
-14.798		
-15.255		
-18.018		
-19.219		
-19.472	-16.7	-14.8
-19.582		
-19.899		
-20.956		-18.1

Table 5. Electronic structure of adsorbed metaphosphacarborane (1,7-$PCB_{10}H_{12}$). The comparison of the semi-empirical ground state theory (PM3-NDO) of the molecular orbitals of a single orthophosphacarborane with experiment. All energies are in eV.

theory: (PM3)	Ag	Au
0.524		
0.127		4.5
0.0688		
-0.089		
-0.093		
-1.030		
-1.120		2.8
-1.218		
-1.391		
-1.656 (LUMO)		1.8
-10.201 (HOMO)		
-10.912		
-11.085	-8	-7.6
-11.138		
-11.143		
-11.310		
-11.604		
-12.011	-8.9	
-12.267		
-13.169		
-13.916		
-14.253	-10.7	-10.4
-14.784		
-14.912		

Table 6. Crystal data and structure refinement for 1,7- $PCB_{10}H_{11}$.

Identification code	1,7_CB10H11	
Empirical formula	C H_{11} B_{10} P	
Formula weight	162.17	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	Pa-3	
Unit cell dimensions	a = 9.7418(14) Å	α= 90°.
	b = 9.7418(14) Å	β= 90°.
	c = 9.7418(14) Å	γ = 90°.
Volume	924.5(2) $Å^3$	
Z	4	
Density (calculated)	1.165 Mg/m^3	
Absorption coefficient	0.214 mm^{-1}	
F(000)	328	
Crystal size	0.5 x 0.5 x 0.25 mm^3	
Theta range for data collection	3.62 to 27.48°.	
Index ranges	-1<=h<=12, -12<=k<=1, -12<=l<=1	
Reflections collected	1434	
Independent reflections	356 [R(int) = 0.0624]	
Completeness to theta = 27.48°	100.0 %	
Absorption correction	Psi-scan	
Max. and min. transmission	0.811 and 0.693	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	356 / 0 / 27	
Goodness-of-fit on F^2	1.141	
Final R indices [I>2sigma(I)]	R1 = 0.0445, wR2 = 0.1288	
R indices (all data)	R1 = 0.0545, wR2 = 0.1369	
Largest diff. peak and hole	0.193 and -0.099 e.$Å^{-3}$	

Table 7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1,7- $PCB_{10}H_{11}$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	5348(1)	9567(1)	1751(1)	43(1)
B(2)	4021(1)	10844(1)	1242(1)	46(1)
C(1)	5348(1)	9567(1)	1751(1)	43(1)
C(2)	4021(1)	10844(1)	1242(1)	46(1)
P(1)	5348(1)	9567(1)	1751(1)	43(1)
P(2)	4021(1)	10844(1)	1242(1)	46(1)

Table 8. Bond lengths [Å] and angles [°] for 1,7- $PCB_{10}H_{11}$.

B(2)-P(2)#1	1.8353(16)
B(2)-C(2)#1	1.8353(16)
B(2)-B(2)#1	1.8353(16)
B(1)-P(2)#2	1.8603(19)
B(1)-C(2)#2	1.8603(19)
B(1)-B(2)#2	1.8603(19)
B(1)-B(2)	1.8605(19)
B(1)-P(2)#1	1.8607(19)
B(1)-B(2)#1	1.8607(19)
B(1)-C(2)#1	1.8607(19)
B(1)-P(1)#3	1.877(2)
B(1)-C(1)#3	1.877(2)
B(1)-B(1)#3	1.877(2)
B(1)-H(1)	0.90(2)
B(2)-H(2)	0.996(19)
P(2)#2-B(1)-B(2)	59.11(5)
C(2)#2-B(1)-B(2)	59.11(5)
B(2)#2-B(1)-B(2)	59.11(5)
P(2)#2-B(1)-P(2)#1	105.96(10)
C(2)#2-B(1)-P(2)#1	105.96(10)
B(2)#2-B(1)-P(2)#1	105.96(10)
B(2)-B(1)-P(2)#1	59.10(5)
P(2)#2-B(1)-B(2)#1	105.96(10)
C(2)#2-B(1)-B(2)#1	105.96(10)
B(2)#2-B(1)-B(2)#1	105.96(10)
B(2)-B(1)-B(2)#1	59.10(5)
P(2)#2-B(1)-C(2)#1	105.96(10)
C(2)#2-B(1)-C(2)#1	105.96(10)
B(2)#2-B(1)-C(2)#1	105.96(10)
B(2)-B(1)-C(2)#1	59.10(5)
P(2)#2-B(1)-P(1)#3	107.10(7)
C(2)#2-B(1)-P(1)#3	107.10(7)
B(2)#2-B(1)-P(1)#3	107.10(7)

B(2)-B(1)-P(1)#3	107.09(6)
P(2)#1-B(1)-P(1)#3	59.70(8)
B(2)#1-B(1)-P(1)#3	59.70(8)
C(2)#1-B(1)-P(1)#3	59.70(8)
P(2)#2-B(1)-C(1)#3	107.10(7)
C(2)#2-B(1)-C(1)#3	107.10(7)
B(2)#2-B(1)-C(1)#3	107.10(7)
B(2)-B(1)-C(1)#3	107.09(6)
P(2)#1-B(1)-C(1)#3	59.70(8)
B(2)#1-B(1)-C(1)#3	59.70(8)
C(2)#1-B(1)-C(1)#3	59.70(8)
P(2)#2-B(1)-B(1)#3	107.10(7)
C(2)#2-B(1)-B(1)#3	107.10(7)
B(2)#2-B(1)-B(1)#3	107.10(7)
B(2)-B(1)-B(1)#3	107.09(6)
P(2)#1-B(1)-B(1)#3	59.70(8)
B(2)#1-B(1)-B(1)#3	59.70(8)
C(2)#1-B(1)-B(1)#3	59.70(8)
P(2)#2-B(1)-H(1)	122.1(12)
C(2)#2-B(1)-H(1)	122.1(12)
B(2)#2-B(1)-H(1)	122.1(12)
B(2)-B(1)-H(1)	122.1(13)
P(2)#1-B(1)-H(1)	123.2(12)
B(2)#1-B(1)-H(1)	123.2(12)
C(2)#1-B(1)-H(1)	123.2(12)
P(1)#3-B(1)-H(1)	122.5(12)
C(1)#3-B(1)-H(1)	122.5(12)
B(1)#3-B(1)-H(1)	122.5(12)
P(2)#1-B(2)-P(2)#2	108.07(8)
C(2)#1-B(2)-P(2)#2	108.07(8)
B(2)#1-B(2)-P(2)#2	108.07(8)
P(2)#1-B(2)-C(2)#2	108.07(8)
C(2)#1-B(2)-C(2)#2	108.07(8)
B(2)#1-B(2)-C(2)#2	108.07(8)
P(2)#1-B(2)-B(2)#2	108.07(8)
C(2)#1-B(2)-B(2)#2	108.07(8)

B(2)#1-B(2)-B(2)#2	108.07(8)
P(2)#1-B(2)-B(1)#1	60.45(6)
C(2)#1-B(2)-B(1)#1	60.45(6)
B(2)#1-B(2)-B(1)#1	60.45(6)
P(2)#2-B(2)-B(1)#1	108.87(6)
C(2)#2-B(2)-B(1)#1	108.87(6)
B(2)#2-B(2)-B(1)#1	108.87(6)
P(2)#1-B(2)-P(1)#1	60.45(6)
C(2)#1-B(2)-P(1)#1	60.45(6)
B(2)#1-B(2)-P(1)#1	60.45(6)
P(2)#2-B(2)-P(1)#1	108.87(6)
C(2)#2-B(2)-P(1)#1	108.87(6)
B(2)#2-B(2)-P(1)#1	108.87(6)
P(2)#1-B(2)-C(1)#1	60.45(6)
C(2)#1-B(2)-C(1)#1	60.45(6)
B(2)#1-B(2)-C(1)#1	60.45(6)
P(2)#2-B(2)-C(1)#1	108.87(6)
C(2)#2-B(2)-C(1)#1	108.87(6)
B(2)#2-B(2)-C(1)#1	108.87(6)
P(2)#1-B(2)-B(1)	60.45(8)
C(2)#1-B(2)-B(1)	60.45(8)
B(2)#1-B(2)-B(1)	60.45(8)
P(2)#2-B(2)-B(1)	60.44(8)
C(2)#2-B(2)-B(1)	60.44(8)
B(2)#2-B(2)-B(1)	60.44(8)
B(1)#1-B(2)-B(1)	109.92(10)
P(1)#1-B(2)-B(1)	109.92(10)
C(1)#1-B(2)-B(1)	109.92(10)
P(2)#1-B(2)-H(2)	122.2(10)
C(2)#1-B(2)-H(2)	122.2(10)
B(2)#1-B(2)-H(2)	122.2(10)
P(2)#2-B(2)-H(2)	121.1(9)
C(2)#2-B(2)-H(2)	121.1(9)
B(2)#2-B(2)-H(2)	121.1(9)
B(1)#1-B(2)-H(2)	121.1(9)
P(1)#1-B(2)-H(2)	121.1(9)

C(1)#1-B(2)-H(2)	121.1(9)
B(1)-B(2)-H(2)	120.4(10)

Symmetry transformations used to generate equivalent atoms:

#1 -z+1/2,x+1/2,y-1 #2 y-1/2,z+1,-x+1/2 #3 -y+3/2,-z+1,x-1/2

Table 9. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for 1,7- $PCB_{10}H_{11}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	41(1)	41(1)	47(1)	1(1)	-1(1)	1(1)
B(2)	47(1)	45(1)	47(1)	4(1)	-4(1)	0(1)
C(1)	41(1)	41(1)	47(1)	1(1)	-1(1)	1(1)
C(2)	47(1)	45(1)	47(1)	4(1)	-4(1)	0(1)
P(1)	41(1)	41(1)	47(1)	1(1)	-1(1)	1(1)
P(2)	47(1)	45(1)	47(1)	4(1)	-4(1)	0(1)

Table 10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for 1,7- $PCB_{10}H_{11}$.

	x	y	z	U(eq)
H(1)	5520(20)	9363(19)	2640(20)	57(6)
H(2)	3472(16)	11330(17)	1950(20)	48(5)

[1] Brint, P.; Sangchakr, B.; McGrath, M.; Spalding, T. R.; Suffolk, R. J. *Inorg. Chem.* **1990**, *29*, 47-52.

[2] Zhang, J.; McIlroy, D. N.; Dowben, P. A.; Zeng, H.; Vidali, G.; Heskett, D. and Onellion, M. *J. Phys.: Condens. Matter* **1995**, *7*, 7185-7194.

[3] Caruso A. N.; Bernard, L.; Xu, B. and Dowben, P. A. *J. Phys. Chem. B* **2003**, *107*, 9620-9623.

[4] Green, T. A. ; Switendick, A. C.; Emin D. *J. Chem. Phys.* **1988,** *89,* 6815-6822.